

ELEMENTS
OF
CHEMICAL ANALYSIS,
QUALITATIVE AND QUANTITATIVE.

BY
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TO

THOMAS GRAHAM, ESQ., F.R.S. L. & Ed.,

PROFESSOR OF CHEMISTRY IN UNIVERSITY COLLEGE, LONDON,
PRESIDENT OF THE CHEMICAL SOCIETY, ETC.

HAD I no other inducement, my dear Sir, in offering you the present work, than your well-merited scientific reputation, ample indeed would that have been; but the personal attention and kindness you have always manifested towards me, constitute not a slight additional incentive to the very small tribute of esteem, the paying of which is now the privilege of

Your late pupil,
and attached friend,

THE AUTHOR.

P R E F A C E.

IN the First Part and division of this work, instructions are offered for performing the ordinary manipulations of analytical processes; to which is added, a description of the mode of preparing and applying the various reagents employed, including the means of detecting the impurities with which these are occasionally contaminated.

The Second Part is devoted to the statement of the appearances produced by the principal reagents when applied to various chemical substances. These appearances constitute the groundwork of a systematic course of operations to be performed in the qualitative examination of every variety of substances, which forms the subject of the Third Part. These instructions include the use of the mouth blowpipe in analysis, the analysis of mixed gases, processes for the detection of poisons in organic mixtures, the analysis of urine and discrimination of urinary calculi.

In the Fourth and last division of this work, quantitative analysis is treated of. The processes are there described by which all bodies which enter into the composition of familiar substances are separated and their weights determined, especial attention being directed to all articles of commercial importance.

This division concludes with a minute account of the operations of organic analysis.

A considerable number of the processes described are those recommended by our two greatest authorities in analytical chemistry — Berzelius and Rose; but several of the processes described are of recent invention, and new to treatises on the subject. Some of these will be found of considerable value.

An Appendix is added, containing a description of processes for the complete analysis of crude potashes and ores of manganese, for the refraction of nitre, the valuation of guano, the analysis of ashes of vegetables, and a note on the analysis of soils. The mode of calculating the atomic constitution of a substance from its per-centage composition, when known, is also described, with the methods of taking the specific gravity of matter in different conditions; and numerical tables are appended, which have been formed to expedite the calculations of analysis.

The considerable enlargement of the present edition is principally caused by the introduction of a much fuller account of the different reagents than the first edition contained, by an amplification of the second and third divisions on the subject of qualitative analysis, and by the introduction of several important processes for the analysis or valuation of various articles of commerce.

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ELEMENTS

OR

CHEMICAL ANALYSIS.

PRELIMINARY OBSERVATIONS.

THE composition of any compound body may be expressed in the simple elements which form its *ultimate constituents*, and also, very frequently, by other and less complex bodies, which, by their immediate union, compose the substance in question, and are its *proximate constituents*. The substance *alum*, for example, is composed of four bodies, themselves compound, namely, *alumina*, *potash*, *sulphuric acid*, and *water*: and each of these proximate constituents is composed again of a pair of elementary bodies; namely, alumina of *aluminum* and *oxygen*, potash of *potassium* and *oxygen*, sulphuric acid of *sulphur* and *oxygen*, and water of *hydrogen* and *oxygen*: therefore the ultimate constituents of alum are aluminum, oxygen, potassium, sulphur, and hydrogen. A chemical analysis may have for its object the separation of either the proximate or ultimate constituents, but most generally of the former, at least in the department of inorganic chemistry. Thus, in an analysis of alum, the alumina, potash, sulphuric acid, and water are the substances sought, and the elementary composition of these bodies being known, the simple elements of which alum is composed are also determined.

An analysis of any substance may be limited to the discovery of the number and nature of its constituents, or the analysis may extend to the determination of the proportion by weight of these constituents. Thus it might be ascertained

that alum contains sulphuric acid, potash, alumina, and water ; or, further, that the salt in question consists, in 100 parts, of 33·78 parts of sulphuric acid, 9·93 of potash, 10·82 of alumina, and 45·47 of water. An examination of the first kind, which does not develop more than the nature or quality of the constituents, is termed a *qualitative analysis* ; while an examination of the second kind, which embraces the quantities of the constituents, is termed a *quantitative analysis*. The qualitative analysis of a substance is therefore independent of, and must necessarily precede, the quantitative analysis of the same body.

The qualitative examination of a substance is very frequently confined to the detection of a single constituent ; for example, to the detection of sulphuric acid in vinegar, and of a specified metal in an ore, all the other bodies which may be present being neglected. In like manner, the quantitative examination of a substance is also often limited to the discovery of the proportion, by weight, of a single constituent, to the neglect of all the others ; for instance, of the proportion of available soda in the impure carbonate of soda, and of the proportion of real peroxide of manganese in the common ore of manganese. Analytical processes for attaining such objects as the latter have acquired considerable importance of late years, from their constant application in estimating the real value of numerous articles of commerce.

For the successful prosecution of the qualitative analysis of a substance, the operator should possess a certain skill in manipulations, and a familiar acquaintance with tests, their manner of application, and the appearances they produce when brought into contact with the substances for which he is seeking. The principal manipulations of qualitative and quantitative analysis will be shortly described separately ; then follow a list of the most important tests, a tabular view of the appearances which certain tests produce with the various substances whose presence is to be sought for, and a description of a systematic course of operations to be pursued in every case where the object is a *complete* qualitative analysis of an unknown substance.

PART I.

MANIPULATIONS AND REAGENTS.

CHAPTER I.

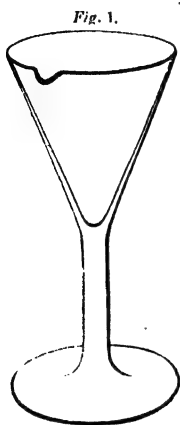
MANIPULATIONS IN QUALITATIVE ANALYSIS.

1. THE ordinary operations of qualitative analysis are exceedingly simple, and easy of execution, usually consisting of little more than merely mixing a reagent with the solution of the substance to be analysed. The *reagent* is so named from its producing, when placed in contact with another substance, a particular appearance or change, the *reaction*, by which the presence of a particular substance is indicated. The reagent is also often referred to as the *test* or *test-liquid*. The appearance which results from the application of the reagent or test to the substance under examination, should always, therefore, lead to a positive conclusion respecting the presence or absence of the ingredient sought for.

2. In all ordinary cases, the reagent is applied in *solution* to the substance to be analysed, the latter being also in a state of solution. The liquid employed for effecting solution (which is named the *solvent*), whether of the reagent or the substance under examination, should be pure distilled water, if the body is soluble in that liquid, unless a special direction is given to the contrary. Substances that are insoluble in water are commonly dissolved in strong acid liquids. For an account of the mode of obtaining solutions of substances insoluble in water, see the remarks at the commencement of the chapter on the analysis of Silicates (Part III.).

The reagents which are freely soluble in water should not be employed in qualitative investigations in the state of *saturated solution*, that is, of a solution containing as much of the substance as it is capable of holding at a given temperature. For use in qualitative analysis, the solutions of the reagents

may contain, in general, one part of the dry substance to twenty or thirty parts of pure water.

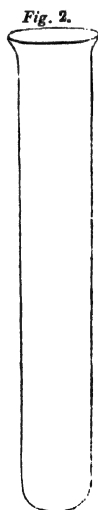


3. The mixture of the solution of the substance to be analysed, and the solution of the reagent may be conveniently made in test glasses, resembling ordinary conical wine glasses, provided with a spout for the convenience of pouring liquids into a tube or flask, with the view of applying heat, an operation frequently necessary. The liquids are mixed in the test glasses by stirring them together briskly with a glass rod. A test glass should be clear and colourless; it should neither run down to a point within, nor should the bottom be flat, but gently rounded. Such a glass is represented in *fig. 1*.

4. If the quantity of material to be operated on is small, the mixture with the reagent may be made on a flat piece of glass, using only one or two drops of the solution of the substance to be analysed, and applying the test from the extremity of a glass rod. The same thing may be done in a watch-glass, where it is necessary to apply heat; or if the reagent produce a change of colour, in a small porcelain capsule, held in any convenient manner over a gas or a spirit-lamp flame.

5. It is advisable, however, in general to operate on small quantities, and to apply the test drop by drop, as it frequently happens that a very different effect is produced by the same reagent when added in large, to what is produced in small quantities; differences which are highly characteristic, and only perceived when the test is applied in a gradual manner.

6. Instead of test glasses, test tubes (*fig. 2.*) are frequently employed, possessing as they do the advantage over glasses of allowing heat to be applied without transferring the liquid into another vessel. A convenient size for ordinary use is five inches in



length, by three quarters of an inch in diameter. The mixture of the two substances must be effected by agitation.

7. The effects exhibited by some particular tests are not immediately perceptible, but are seen only after a certain time has elapsed: in such a case the mixture containing the reagent must be allowed to stand a few minutes, a mark distinguishing what test has been added being applied to prevent mistakes.

8. The effect which follows the application of a reagent to the solution of the substance under examination, from which effect a conclusion concerning the composition of the substance is to be drawn, is in most cases the production of a *precipitate*; in some instances, effervescence, that is, the disengagement of bubbles of a gas, and in others the development of a particular odour or colour. Precipitation is the process of producing a solid from a liquid, commonly in a sudden and not in a gradual manner, and as a result of the addition of another substance to the liquid. The separated solid is termed the precipitate, whether it subsides to the bottom, rises to the surface, or remains diffused through the liquid. Crystallization also consists in the production of a solid out of a liquid, but the latter process differs from precipitation in the deposition of the solid body being gradual and consequent on the removal, by evaporation, of the liquid by which it was held in solution.

Precipitates are distinguished according to their appearance, as curdy, gelatinous, crystalline, flocculent, pulverulent, &c. When solutions of common salt and nitrate of silver are mixed together, a *curdy* precipitate falls, consisting of chloride of silver; solution of alum with ammonia gives a *gelatinous* precipitate of alumina; solution of chloride of potassium with a strong solution of tartaric acid, in excess, gives a *crystalline* precipitate of bitartrate of potash (cream of tartar); a dilute solution of the persulphate of iron with ammonia gives a *flocculent* precipitate of the peroxide of iron; and a solution of acetate of lead with sulphuric acid gives a *pulverulent* precipitate of sulphate of lead.

9. It is often necessary in qualitative analysis to ascertain

the action of a test liquid on a precipitate which has been produced in the course of testing; this may, in general, be done in the same test glass or tube in which the first testing was performed, the supernatant liquid, if the precipitate subsides readily, being poured off. Stirring with a glass rod, and the application of heat, frequently assist the subsidence of a precipitate. When the supernatant liquid contains something in solution which interferes with the action of the liquid to be added, the precipitate must be collected on a filter and washed with distilled water, until perfectly cleaned from the interfering substance. This can be performed by means of a small paper filter held in a glass funnel, some appropriate test being applied to ascertain when the liquid which passes through the filter is perfectly pure. The precautions to be observed in the process of filtration are described in the following Section, on the ordinary manipulations of quantitative analysis.

One of the most useful instruments of research in qualitative analysis is the mouth blow-pipe; a chapter of the Third Part of this work is devoted to an account of the manner of using this instrument.

CHAPTER II.

MANIPULATIONS IN QUANTITATIVE ANALYSIS.

10. The manipulations of quantitative analysis are, in general, equally simple as those of qualitative analysis, but require to be performed with extreme care and attention. The ingredient whose amount is to be ascertained is commonly either

(1.) *Separated from its solution in the solid form by precipitation; or*

(2.) *It is expelled in a volatile state from a known weight of the material to be analysed; or*

(3.) *Its amount is determined by observing what quantity is required of another substance to produce a given effect on the ingredient to be estimated; or*

(4.) *Being in solution associated with none but volatile substances, it is separated by evaporation to dryness.*

11. In cases of the first kind, a known weight of the substance to be analysed is obtained in a state of solution; and the constituent whose amount is to be determined, after being precipitated in the solid state, all the other constituents remaining in solution, is collected with several precautions, and obtained in a fit state to be weighed. In this manner, for example, the quantity of oxide of copper contained in sulphate of copper (blue vitriol) is determined. The sulphate of copper is dissolved in hot water, and caustic potash in excess is added to the hot solution to precipitate black oxide of copper, which is collected on a filter and dried with certain precautions, and weighed.

12. In cases of the second kind, the weight of the original substance being known, the weight of the particular ingredient can be ascertained from the loss of weight which occur on its expulsion. Sometimes the volatilized substance is re-collected and procured in a state fit to be weighed. For examples of processes of this nature, see the modes of estimating

carbonic acid in carbonates, water in hydrates, and ammonia in ammoniacal salts, and the processes of organic analysis.

13. In analytical processes of the third kind, the substance to be analysed is mixed with a reagent capable of producing a certain obvious change on the particular ingredient to be estimated, the amount of which is known by the quantity of the reagent necessary to be applied in order to complete the change. For example, the quantity of real alkali contained in a solution of soda-ash is ascertained by the quantity of dilute sulphuric acid of known strength, necessary to be applied to the soda to destroy its alkaline re-action on test-paper. (See the processes of alkalimetry and chlorimetry; and for other examples of operations of this kind, see the valuation of ores of manganese and copper ores, and a process for ascertaining the amount of sulphur in sulphureous mineral waters).

14. One or more of the constituents of a compound body having been already separated by precipitation, only one non-volatile substance remaining in solution, the weight of the latter is frequently obtained by evaporating the solution to dryness, and weighing the fixed residuc. In this manner, the fixed alkalies, potash and soda, are commonly estimated. (See also a process for the analysis of brass, in which the zinc is estimated in this way.)

15. The amount of one ingredient can also be estimated indirectly when the whole quantity of the other ingredients has been obtained, the loss or deficiency on the original weight then evidently representing the proportion present of that particular substance.

By far the larger number of analytical operations are of the first description; that is, a substance is separated in the solid state from a solution of the material operated on. General directions for the performance of such operations only will be given at present; the manipulations for the others will be described afterwards, when treating of the particular substances to which such operations refer.

16. Precipitation from a solution is the means usually employed to obtain an ingredient of a compound in a solid or

fixed form. The original combinations of the material to be analysed, or of the substances into which it may be converted by the act of solution, are then broken up: each particular ingredient whose amount is the object of inquiry being either (1.) combined with another substance, and forming a new insoluble compound (in which it is contained in known proportions, and which is capable of being weighed), or (2.) being in its own natural condition insoluble, although held in solution by the substance to which it was united in the material under examination, that combination is destroyed, the ingredient assumes its natural insoluble condition, and is therefore precipitated. Thus, in the analysis of chloride of mercury (corrosive sublimate), for instance, to obtain the proportion of *chlorine*, the chloride of mercury is dissolved in water, and nitrate of silver added to the solution. The combination of mercury with chlorine is thus destroyed, not a particle of chloride of mercury remaining, if sufficient nitrate of silver has been added. The chlorine unites with silver, forming a new insoluble compound, chloride of silver, capable of being weighed, and containing constant and known proportions of chlorine and silver. Next, to obtain the *mercury*, to a solution of the chloride of mercury, protochloride of tin is added. The original combination of mercury with chlorine is, as before, broken up; the protochloride of tin acquiring all the chlorine of the chloride of mercury, that metal is set free, precipitates, and may be collected and weighed. From the weight then of the chloride of silver (100 parts of which contain 24.67 parts of chlorine), the amount of chlorine becomes known: the mercury is ascertained by direct weighing.

17. The first point to be attended to in precipitation is, that both the solution of the substance to be analysed, and of the precipitant or reagent employed, be made perfectly clear by filtration through paper; for it is obvious that any solid matter diffused through either of the solutions would be carried down by, and afterwards separated with, the precipitate whose weight is to be ascertained, thus producing a fallacious result.

18. To add precisely the proper quantity of the precipitant is difficult, but rarely necessary, as an excess in most cases produces no greater inconvenience than a little longer washing on the filter: to be assured that a sufficiency has been added, the precipitate must be allowed to subside, and the reagent dropped carefully into the supernatant liquid, when it will be seen whether an additional precipitate is formed or not. If a precipitate is formed, of course a further quantity of the precipitant must be added, and the examination repeated.

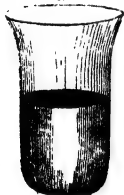
19. The subsidence and aggregation of a precipitate are favoured in various ways: the most usual is by heating the liquid; so advantageous, indeed, is this means, that it would be advisable to follow as a general rule, always to precipitate while warm, and to boil the liquid gently for a few minutes after precipitation. Next to heating, agitation with a glass rod, and the addition of an acid or an alkali, are the means usually adopted; but the employment of the latter must be guided by the nature of the particular substances operated on.

Fig. 3.



glass beaker vessel,

Fig. 4.



When heat is to be applied, a convenient vessel to perform the precipitation in, is a porcelain bason, not very shallow, having a capacity of about twelve or fourteen ounces (*fig. 3.*). A glass beaker vessel, that is, a jar thin at bottom and with a spreading edge at top (*fig. 4.*), is also very useful for applying heat; but where heat is not requisite, a common glass tumbler, having a spout for convenience in pouring from, may be employed. It will be found useful to have different sizes of these tumblers and beakers. It is unnecessary for the bottoms of the tumblers to be more than one eighth of an inch thick.

20. The next operation in order is *filtration*. This is done by means of a paper filter, formed by doubling twice a circular piece of filtering paper so as to form a quadrant, and

then opening one of the folds, as shown in *fig. 5*. The filter is supported in a glass funnel, which is itself held in any convenient manner, a vessel being placed below the funnel to receive the filtered liquid.* Before pouring the turbid liquid on it, the filter should be wetted with a few drops of distilled water, without which precaution the liquid would not at first pass through clear. As the loss of a single drop of the liquid might render the operation worthless, its transference to a filter must always be directed by a glass rod applied to the lip of the containing vessel, and held nearly perpendicular, with its extremity very near but not touching the filter (*fig. 6*).

Fig. 5.

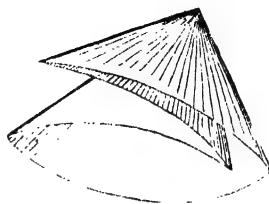


Fig. 6.



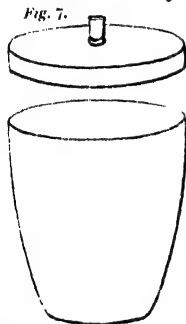
21. It invariably happens in precipitations, that the precipitate carries down with it a sensible quantity of the soluble salts present in the solution (the precipitant for instance), so that to obtain the precipitate in a pure state, not only must the liquid itself be washed from the solid precipitate with pure distilled water, but the washing requires to be continued long after the solution has passed

through, in order to remove all the soluble salt attached to the precipitate. This is done most effectually by hot water, an appropriate reagent being occasionally applied to the washings to ascertain whether the salts are still being washed out. A delicate indication of the presence of any salt which is not volatile, is afforded by evaporating a few drops to dryness on a clean piece of platinum foil, a minute trace of the salt

* An excellent filtering paper is sold by Messrs. R. Griffin and Co. of Glasgow, from whom filters of various sizes, already cut, may also be procured. They likewise supply all the other articles required in analysis.

causing a very perceptible stain, which could not occur with pure distilled water. So long as this stain is observed, the washing must be continued. There are a few precipitates which, being slightly soluble, must not be washed for a continued length of time: the cases in which this precaution is necessary to be observed will be mentioned subsequently.

22. Supposing the washing complete, the next step is to obtain the precipitate in a state of perfect dryness, which, if the substance is not volatile or decomposable at a high temperature, is effected by ignition at a red heat. Before ignition, however, it must be dried as completely as possible, without removing from the filter, at a temperature of about 180° or 200° Fahr., in an oven or drying stove, or in a plate on the sand-bath. This done, the substance to be weighed must be transferred to a small crucible, the weight of which is ascertained immediately before using, and which should not exceed 300 or 400 grains, that the delicacy of the balance may not be impaired. For ordinary use, a small

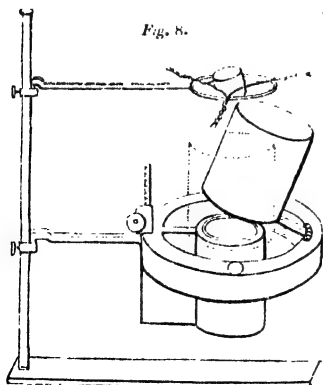


platinum crucible (*fig. 7.*) is by far the most convenient, a common spirit lamp with a large flame affording in general a sufficient degree of heat. When a substance is to be ignited which might corrode platinum*, a crucible of Berlin porcelain is employed. The transference of the precipitate to the crucible, without losing the minutest portion, is the most delicate part of the whole operation. Place the crucible, with its lid removed, in the centre of a sheet of highly glazed coloured paper; with the assistance of a clean platinum spatula transfer the bulk of the precipitate to the crucible, and

* Platinum vessels must never be made use of when the subject of operation is a metal, a caustic alkali, nitre, sulphur, or a sulphuret; nor should any metallic compound easy of reduction, or a phosphate, be heated in a platinum crucible when organic matters are also present. Contact with lead and organic compounds containing lead should be most scrupulously avoided. When heated in a fire-place, the platinum crucible should not be exposed naked to the fire, but be enclosed in an earthen crucible, as the ashes of the coal or coke exert a very injurious action on platinum vessels, the platinum combining with the silicon in the ashes to form a silicuret of platinum.

hold the filter by means of a forceps at that part which, being folded, contains none of the precipitate, immediately over the crucible. Apply a light to the filter, and burn it completely, allowing the precipitate to fall into the crucible, and so regulating the combustion that the flame shall reach last that part of the filter held by the forceps, otherwise (unless the crucible be large enough to retain it) it will fall on the glazed paper while burning. In this way, it sometimes happens that the filter may be completely burned, although more frequently a carbonaceous residue remains, which must be afterwards burned by allowing air to have access, by lifting the cover when the crucible has obtained a full red heat.

The mode of applying heat may depend greatly on the convenience of the operator. It has been stated, that if a small platinum crucible is employed, the temperature afforded by an ordinary spirit lamp is sufficient. In other cases the heat of an open fire, of a stove, of a spirit lamp with a double current of air, or of an inflammable mixture of air and coal gas, is more convenient. If an open furnace or stove be employed, the crucible, whether of platinum or of porcelain, should never be introduced naked into the fire, but always be enclosed in a Cornish or Hessian crucible. The spirit lamp with double current of air, or Rose lamp, is a very ready means of obtaining an intense heat (*fig. 8.*).



The principle of its construction is the same as that of the Argand oil lamp, a current of air being supplied to the interior as well as to the exterior of the flame. In the figure, the chimney is represented attached to the lamp by a hinge, by which means ready access to the wick is obtained for the purpose of trimming. The only objection to the use of

this lamp is the large quantity of spirit it consumes.

Where coal gas can be commanded, an excellent source of heat is the combustion of an inflammable mixture of gas and air, which affords a degree of heat equal to that produced by the Rose lamp, at a much less expense. The mixture of gas and air is made in the chimney; a wire gauze is fastened over the top, above which the inflammable mixture is ignited. The annexed cut (*fig. 9.*) represents the entire

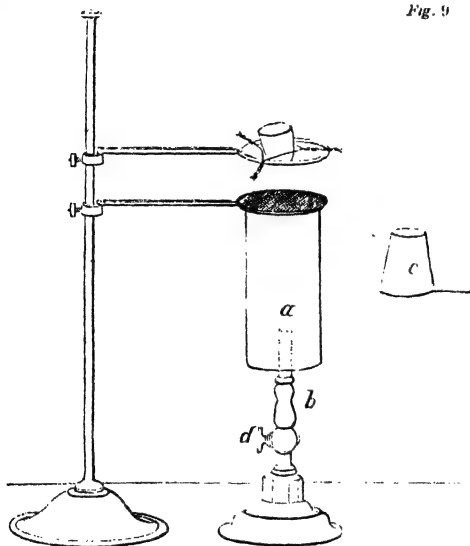


Fig. 9

arrangement: *a* is a copper chimney supported by a retort ring, having a ridge or pegs for this purpose on the outside: the bottom is open to admit air; *b* is the gas jet, the extremity of which is near the bottom of the chimney. The crucible to be ignited is supported over the flame on a triangular piece of iron

wire placed on another ring of the retort stand; *c* is a second chimney or jacket to be placed over the crucible to create a constant and equal draught. The proportion of gas and air is regulated by the stopcock *d*, and by raising or depressing the chimney over the extremity of the gas jet. The flame should not burn yellow, but with a clear blue colour, and ought not to produce any deposit of carbon on a solid held in it. A little experience will show what kind of flame produces the most intense heat.

If the filter has been completely burned, a few minutes' exposure to a red heat is all that is farther necessary. The crucible may then be removed, allowed to become quite cold with its cover still on, and weighed. The weight of the empty crucible must be ascertained, both immediately before

and after the ignition: if any appreciable difference exists in the two weighings, and its cause is not obvious, the analysis must be rejected.

23. The ash of the filter in which the precipitate was collected has been weighed with the latter, for which an allowance must obviously be made. If the weight of the ash was not previously known, a similar filter to the one used may be burned, and the ash weighed by itself, or placed with the weights in the opposite pan of the balance. The most convenient way is to use filters of particular sizes and weights, and to have previously ascertained the proportion of ash contained in the paper by burning a known weight, calcining the residue in a platinum capsule, and weighing.

24. Such is the course to be adopted in the drying and ignition of precipitates which are not volatile at a red heat. When, on the contrary, the precipitates are volatile, as for instance, calomel and sulphuret of mercury, or when they undergo partial decomposition at a high temperature, a different routine must be followed. The filter in which the substance is collected must then be weighed before filtering, and the substance and filter weighed together after drying; but some precautions are required to do this with accuracy. Before a filter is weighed, it must be rendered perfectly dry by holding it a few minutes near the fire; it is then introduced folded, either into a platinum crucible carefully closed with its lid, or into a glass tube sealed at one end, and closed at the other with a cork, the outside of which is coated with sealing-wax. This being weighed, the filtration may be proceeded with. The precipitate and filter, washed, and dried in an oven at a temperature of about 200° , or in a water-bath at 212° , is introduced into the same crucible or tube and weighed. After a second heating, if the weight be the same as at first, the substance may be considered as dry; if not, the heating must be continued until the weight becomes constant. The increase on the original weight of the filter and containing vessel gives, of course, that of the substance.

Such are the general directions which may be given for the performance of the ordinary operations of precipitation, fil-

tration, and ignition. But there are many analytical operations which must be performed in a manner entirely different from what has been described; and others, in which a modification merely of the process is necessary. These, however, are so numerous and varied, that a description of the manipulations of each method would constitute almost an entire description of the processes, which must necessarily be reserved for that portion of the work which treats of actual analysis. We proceed, then, to the consideration of those characters of chemical substances by which they may be distinguished from each other, or to the subject of qualitative analysis. Before studying these characters, however, it will be necessary to notice the principal reagents employed, their ordinary impurities, and the manner of obtaining them in a state of purity

CHAPTER III.

REAGENTS.

REAGENTS or tests are substances which are employed to determine the presence of other bodies by the production of a particular appearance which attends the mutual action of the reagent and the other substance. If this appearance is well marked, and exhibited only when two definite bodies are placed in contact with each other, the presence or absence of one of them in a given mixture may obviously be proved by the application of the other. When, for example, a solution of the yellow prussiate of potash is placed in contact with a solution containing the peroxide of iron, a deep blue precipitate is formed consisting of Prussian blue, the colour of which is instantly destroyed on mixing the precipitate with an excess of a caustic alkali, but is not affected by acids, though but slightly diluted. Now, a precipitate possessed of these characters is formed only on the admixture of prussiate of potash with a solution containing iron; hence either of these substances serves as a reagent for detecting the presence of the other.

Reagents must, in general, be used only in a state of perfect purity, otherwise the conclusions to which they lead may be fallacious. The manner of ascertaining the presence of those impurities which are most likely to contaminate reagents, from the manner of their production, are pointed out in the following description of the most important of those bodies. The reagents here noticed are the following:—

- | | |
|-------------------------|--------------------------|
| 1. Sulphuric acid. | 7. Oxalic acid. |
| 2. Hydrochloric acid. | 8. Acetic acid. |
| 3. Nitric acid. | 9. Potash. |
| 4. Nitro-muriatic acid. | 10. Carbonate of potash. |
| 5. Tartaric acid. | 11. Carbonate of soda. |
| 6. Sulphurous acid. | 12. Ammonia. |

- | | |
|---------------------------------|--------------------------------|
| 13. Carbonate of ammonia. | 26. Antimoniate of potash. |
| 14. Oxalate of ammonia. | 27. Muriate of ammonia. |
| 15. Sulphuretted hydrogen. | 28. Caustic barytes. |
| 16. Hydrosulphate of ammonia. | 29. Chloride of barium. |
| 17. Chloride of platinum. | 30. Nitrate of barytes. |
| 18. Phosphate of soda. | 31. Acetate of lead. |
| 19. Yellow prussiate of potash. | 32. Nitrate of silver. |
| 20. Red prussiate of potash. | 33. Ammonio-nitrate of silver. |
| 21. Infusion of galls. | 34. Iodide of potassium. |
| 22. Chromate of potash. | 35. Sulphate of indigo. |
| 23. Protochloride of tin. | 36. Starch. |
| 24. Chloride of lead. | 37. Test papers. |
| 25. Sulphate of lime. | 38. Water. |

1. *Sulphuric acid*. — In qualitative analysis, sulphuric acid is occasionally used as a solvent for bodies insoluble in water, but principally for the detection of barytes, lead, and strontian, which are precipitated from their solutions by sulphuric acid; and for the detection of many acids which are liberated from their combinations with bases by sulphuric acid, by virtue of the stronger affinity of the latter for the bases. The concentrated acid (oil of vitriol) should be diluted with eight or ten measures of distilled water, when required as a test for barytes, lead, and strontian. For other purposes, sulphuric acid is sometimes employed in a concentrated, and sometimes in a diluted state.

The impurities with which commercial sulphuric acid is apt to be contaminated are nitric acid, sulphate of lead, arsenious acid, and oxide of tin. If the acid, when boiled with a few drops of a solution of sulphate of indigo (page 36.), does not discharge the colour of the latter, the absence of nitric acid may be inferred. Oil of vitriol ought not to become turbid when diluted with five or six times its bulk of water. If it does, this arises from sulphate of lead, which is soluble in the strong, but not in the dilute acid. By dilution and subsidence, the sulphate of lead can be removed, and the acid used as a test for most purposes. If the diluted and decanted acid affords a precipitate when exposed to sulphuretted hydrogen gas, this may be due to the presence of arsenious acid and protoxide of tin; arsenious acid produces a yellowish, and protoxide of tin a dark brown precipitate. For

other means of discovering the presence of arsenious acid, see the chapter on the detection of poisons.

When sulphuric acid is required pure, and in a concentrated state, it is best obtained by distilling oil of vitriol, the portions which first distil over being rejected until they are found to be free from nitric acid by the test of sulphate of indigo.

2. *Hydrochloric acid*.—This acid is extensively used in qualitative analysis, as the solvent for minerals and other substances insoluble in water; and as a special reagent, it is used for the detection of silver and sub-oxide of mercury. For the latter purposes, a solution of common salt (chloride of sodium) may frequently be substituted for hydrochloric acid. (See also Chloride of Lead, 24.)

The hydrochloric acid of commerce is always contaminated with impurities which render it quite unfit for general use as a reagent. The impurities always present are sulphuric acid and iron; besides these there are sometimes found sulphurous acid, free chlorine and arsenic. The presence of sulphuric acid is indicated by the production of a precipitate when a few drops of a solution of chloride of barium are added to the acid. If the acid, after being first neutralised with ammonia, becomes black on the addition of hydro-sulphate of ammonia, it contains iron. If sulphurous acid is present, the acid, after being heated with a little nitric acid to convert the sulphurous acid into sulphuric acid, affords a precipitate with chloride of barium. The presence of sulphurous acid may also be easily detected by saturating the hydrochloric acid with carbonate of soda, then adding a little solution of starch and a few drops of a solution of iodate of potash or soda, after which some sulphuric acid is applied by drops to set free iodic acid, and, if present, sulphurous acid: these acids react on each other with liberation of iodine, which is immediately recognized by the production of a blue colour with the starch. The absence of a blue colour is therefore an indication of the absence of sulphurous acid. To discover the presence of free chlorine in hydrochloric acid, the latter is boiled with a few drops of a solution of sulphate

of indigo, the blue colour of which is discharged by a very minute quantity of free chlorine at the boiling temperature, but is not affected by pure hydrochloric acid. Free chlorine and sulphurous acid are never found together in hydrochloric acid. If the acid contains arsenic, it affords a yellowish precipitate when exposed to sulphuretted hydrogen gas; but if it is pure, that gas produces no effect on it whatever. (See the modes described for the discovery of arsenic in the chapter headed "Detection of Poisons.")

Another test to which hydrochloric acid should be subjected before being used in analysis, is evaporation to dryness, to ascertain whether it leaves a fixed residuc. For this purpose, a drop or two of the acid may be placed on a piece of platinum foil which is held in the flame of a spirit lamp until dry. The pure acid volatilizes completely, but the commercial acid leaves a fixed matter, consisting usually of sulphate of soda and oxide of iron.

Pure hydrochloric acid may be conveniently prepared by gently heating in a retort a mixture of eight ounces of the best patent salt with ten measured ounces (that is, a measure equal to ten ounces of water) of oil of vitriol of sp. gr. 1.650, free from nitric or nitrous acid*, and conducting the hydrochloric acid gas, then disengaged, into a vessel containing ten ounces of distilled water. The receiver should be kept as cool as possible by the external application of cold water; the beak of the retort should be raised so as to prevent any of the mixture of salt and sulphuric acid from falling into the receiver, and the hydrochloric acid gas should be conducted into the receiver from the end of the beak of the retort by a bent tube, just long enough to reach to the surface of water in the receiver. For ordinary purposes the product may be diluted with water until its specific gravity is 1.11.

3. *Nitric acid.* — The principal use of nitric acid in analysis is as a solvent of substances which are insoluble in water,

* If the sulphuric acid is contaminated with nitric or nitrous acid, the hydrochloric acid obtained by it contains free chlorine. All the chlorine, however, will be contained in the first products that come over, which may be received separately.

particularly sulphurets and metals; which it converts into oxygenated products possessed of solubility.

The nitric acid of commerce is generally contaminated with sulphuric acid and chlorine; the former is detected by the production of a white precipitate when a drop or two of a weak solution of nitrate of barytes is added to the diluted acid; and the chlorine is detected by the formation of a white precipitate with a solution of nitrate of silver. If the acid is pure and diluted, no change is produced on the application of either of these reagents. When evaporated on a piece of platinum foil, nitric acid should leave no residue.

Pure nitric acid may be easily procured from the acid of commerce by adding a little nitre to arrest the sulphuric acid present, and then gently distilling in a retort nearly to dryness. All the chlorine comes over with the first products, and should be received separately from the remainder. If nitric acid contaminated with chlorine is heated in an open vessel the chlorine is expelled almost before the acid begins to volatilize. The brownish tinge which nitric acid often possesses, is due to the presence of nitrous acid, which may also be removed by boiling, if necessary; but it rarely happens that the presence of nitrous acid is an inconvenience.

4. *Nitro-muriatic acid*, or *aqua regia*. — This acid, which is prepared by simply mixing about three measures of pure hydrochloric acid with one measure of pure nitric acid, is the most powerful solvent we possess for the generality of metals and sulphurets. When nitric and hydrochloric acids are brought together, decomposition ensues, with production of water, hyponitric acid, and free chlorine: this mutual decomposition of the nitric and muriatic acids is suspended when the liquid is saturated with chlorine, but immediately recommences if the chlorine is removed by the application of heat, or by the introduction of a substance capable of absorbing free chlorine.

A mixture of chlorate of potash and dilute muriatic acid, which also yields free chlorine, may often be advantageously substituted for *aqua regia*; in effecting the solution of sulphurets, for instance.

5. *Tartaric acid*. — Tartaric acid is principally used as a means of distinguishing between potash and soda, as it produces a sparingly soluble precipitate in solutions of potash salts, but none in solutions of soda salts. The usual impurities of tartaric acid, as met with in commerce, are sulphuric acid and a salt of lime. A moderately dilute solution should not produce in salts of barytes a precipitate insoluble in nitric acid; nor should oxalate of ammonia cause a precipitate after the acid has been neutralized by ammonia. Tartaric acid is purified by re-crystallization.

6. *Sulphurous acid*. — Through the strong disposition of sulphurous acid to unite with oxygen and become converted into sulphuric acid, it is frequently used as a powerful deoxidizing agent, and as such, finds applications in analysis, both qualitative and quantitative. Some sulphites of metallic oxides, when their solutions are boiled, are completely decomposed, and the whole of the metallic oxide is precipitated, while other sulphites in the same condition remain wholly in solution. On this circumstance are founded processes for the quantitative separation of one class of metallic oxides from another class. In cases where the introduction of a free acid is not admissible, sulphite of ammonia may be employed instead of sulphurous acid.

Sulphurous acid is applied in the state of a solution in water, prepared by heating in a flask half an ounce of powdered charcoal with three ounces, by measure, of oil of vitriol, and conducting the evolved mixture of carbonic acid and sulphurous acid gases through a tube into a bottle of cold water, until the water is saturated with the sulphurous acid. The solution should be preserved from exposure to the atmosphere as much as possible, and never be used unless it possesses a powerful odour of sulphurous acid.

7. *Oxalic acid*. — Oxalic acid is principally used for the detection and estimation of lime, which it precipitates completely from its solutions, if the stronger acids, hydrochloric and nitric, are not present in the free state. Other earths besides lime are precipitated by oxalic acid; but the pre-

precipitates with these, unlike that with lime, are soluble in an excess of oxalic acid.

Oxalic acid is impure if it deliquesces or leaves a fixed residue on ignition. Its crystals should be colourless; their solution should give no precipitate with a diluted solution of a salt of barytes (sulphuric acid), nor should it bleach a dilute solution of sulphate of indigo, when boiled with that reagent (nitric acid). Commercial oxalic acid may easily be rendered perfectly pure by two or three crystallizations, the mother liquors being rejected. (See Oxalate of Ammonia, 14.)

8. *Acetic acid*. — Acetic acid is principally used as a solvent, and for acidulating solutions, in cases where a stronger acid, as hydrochloric, could not be properly applied. Before being used in analysis, acetic acid, if commercial, should be tested with a dilute solution of nitrate of silver for hydrochloric acid, with chloride of barium for sulphuric acid, by boiling with sulphate of indigo for nitric acid, and with chloride of barium after being boiled with nitric acid for sulphurous acid. It should leave no residue on evaporation, and should yield no precipitate when mixed with an excess of an alkaline carbonate.

9. *Potash*. — When a solution of caustic potash is mixed with a solution containing almost any metallic or earthy salt, the base is precipitated through the affinity of the potash for the acid previously in combination with the precipitated base, which may often be recognized merely by a peculiarity in its colour. Of the bases thus precipitated, several may be completely re-dissolved on applying an excess of the alkali, as alumina, oxide of chromium, and oxide of zinc; while others, as oxide of copper, oxide of iron, and oxide of bismuth, remain undissolved, whatever amount of excess of potash is applied. One of these classes of bases may therefore be separated from the other class by means of potash.

To prepare a solution of caustic potash, two parts of carbonate of potash are dissolved in twenty parts of water, and the solution is boiled in a covered iron vessel with one part of lime, weighed as quicklime, but slaked with water before being mixed with the carbonate of potash. After boiling for

about a quarter of an hour, if a portion of the clear liquid from which the carbonate of lime has subsided or been separated by filtration, effervesces when poured into muriatic acid, a little more lime may be added, and the boiling be continued until effervescence with muriatic acid ceases; the carbonate of lime is then allowed to settle, and the clear supernatant liquid is decanted for use.

Solution of caustic potash is usually contaminated with carbonate of potash, sulphate of potash, and chloride of potassium. If it contains carbonate of potash, it effervesces when saturated with an acid. After being neutralized with nitric acid, it ought not to give a precipitate with nitrate of silver, nor with nitrate of barytes. By evaporation until of the specific gravity 1.250, all the sulphate of potash is deposited: the supernatant liquid, decanted, may be diluted for general use; but it will then probably contain some carbonate. If required absolutely pure, it must be made from carbonate of potash prepared from the bicarbonate or the bitartrate of potash.

A solution of *caustic soda*, prepared in the same manner as caustic potash, from two parts of crystallized carbonate of soda, one part of quicklime, and eight or ten parts of water, may be employed for all the purposes to which caustic potash is applied as a reagent.

10. *Carbonate of potash*. — Carbonate of potash is even a more extensive precipitant of bases than caustic potash, and does not, with very few exceptions, re-dissolve the bases at first precipitated by afterwards applying an excess of the carbonate, in the same manner as caustic potash does. The precipitates produced by carbonate of potash in metallic and earthy solutions, are, in general, carbonates of the metallic oxides and earths, but sometimes the oxide or earth itself is precipitated: the latter is the case, for instance, with peroxide of iron and alumina.

The impurities with which commercial carbonate of potash is generally contaminated are alkaline sulphates and chlorides, silica and alumina. The tests of purity are, after being neutralized with nitric acid, nitrate of silver (chlorine), and a

soluble salt of barytes (sulphuric acid). If the neutralized solution, when evaporated to dryness, and the residue treated with water, leaves white flocks or a gelatinous substance undissolved, this is silica. If alumina is present, the neutralized solution will give a white precipitate with carbonate of ammonia.

Pure carbonate of potash is best prepared by calcining cream of tartar (the bitartrate of potash) in an iron pan, lixiviating the residue, and evaporating the clear liquid to dryness.

11. *Carbonate of soda.* — The applications of carbonate of soda in humid analysis are the same as those of carbonate of potash. Carbonate of soda is also much used in analysis by the blowpipe. (See the chapter on the Use of the Blowpipe in Analysis.)

Besides sulphates and chlorides, which are detected as just described, carbonate of soda may contain an alkaline sulphuret, sulphite and hyposulphite. When neutralized with an acid, no white precipitate of sulphur should be produced; the gas evolved on adding sulphuric acid should be perfectly inodorous, and a solution of acetate of lead should afford with the carbonate a perfectly white, and not a brown precipitate.

Pure carbonate of soda is best prepared by heating the bicarbonate for a short time to incipient redness.

12. *Ammonia.* — Ammonia is the reagent most generally employed for the precipitation of bases from their solutions in acids. Some of the bases precipitated by ammonia are redissolved on applying an excess of that reagent, as oxides of copper, silver, and zinc, which may thereby be separated from those bases which are insoluble in an excess of ammonia, as oxides of iron, bismuth, and lead. Solutions containing magnesia, protoxide of manganese, and some other bases, afford a precipitate with ammonia, if they are neutral, and contain little or no ammoniacal salt; but not if they contain much free acid, a soluble double ammoniacal salt being formed in the latter case. The addition of a salt of ammonia to the neutral solution also prevents the precipitation of such bases by ammonia.

Ammonia sometimes contains muriate, carbonate, and sulphate of ammonia, chloride of calcium, and, very rarely, a trace of oxide of tin. The solution should be limpid and colourless: after being neutralized by nitric acid, it should neither be precipitated by nitrate of silver nor by chloride of barium, and should leave no fixed residue on evaporation. The *liq. ammoniæ* of the shops, however, is generally pure.

13. *Carbonate of ammonia*. — The applications of carbonate of ammonia are much the same as those of carbonate of potash, the former being preferred in cases where the introduction of a fixed base would be inconvenient. A few bases capable of being precipitated by carbonate of potash are not precipitated by carbonate of ammonia, especially in the presence of another ammoniacal salt, or a free acid, a soluble double salt of ammonia and the other base being formed.

The impurities occasionally present in carbonate of ammonia are the same as those in ammonia.

For use, as a reagent, one part of the sublimed carbonate of ammonia, which is a sesquicarbonate, should be dissolved in about three parts of water, and this solution be mixed with about one part of solution of ammonia, of ordinary strength, to make the neutral carbonate.

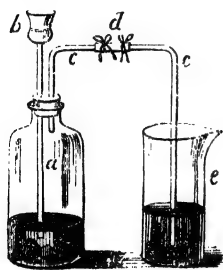
14. *Oxalate of ammonia*. — This reagent, like oxalic acid, is principally used for the detection and estimation of lime, which it precipitates completely from neutral solutions in the form of oxalate. For this purpose oxalate of ammonia is preferable to oxalic acid; as the latter, when mixed with a solution of lime previously neutral, liberates a free acid, which in most cases retains a small quantity of oxalate of lime in solution. Oxalate of ammonia, on the contrary, liberates no acid in precipitating lime from neutral solutions.

Oxalate of ammonia is prepared by dissolving pure oxalic acid in water, adding a slight excess of carbonate of ammonia, and evaporating to obtain crystals. For general use, one part of the oxalate may be dissolved in about twenty parts of water.

15. *Sulphuretted hydrogen*. — This important reagent is

used for the separation of one class of metals from another class, when both exist together in the same solution, and also for the detection and estimation of individual metals. When sulphuretted hydrogen gas is transmitted through an *acid* solution of certain metallic oxides, a double decomposition of the sulphuretted hydrogen and metallic oxide occurs, with formation of water and sulphurets of the metals; the latter, being insoluble, are precipitated. Certain other metals, however, are not precipitated by sulphuretted hydrogen from their *acid* solutions, but only when the acid is neutralized by an alkali; hence sulphuretted hydrogen when applied to a solution of several metals, containing a free acid, precipitates one class, and leaves another class in solution unacted on.

Sulphuretted hydrogen gas is most conveniently prepared by acting on the protosulphuret of iron by dilute sulphuric acid in a bottle fitted up with tubes passing through the cork, as



shown in the annexed figure: *ab* is a funnel tube for pouring in the sulphuric acid; *cc* is a tube in two pieces (joined together by a caoutchouc tube, *d*) for conveying the evolved gas into the solution to be tested, which is contained in the bottle, *e*. The protosulphuret of iron employed in this process may be made by projecting into a red-hot earthen crucible an im-

timate mixture of six parts of flowers of sulphur and nine parts of iron filings. The mixture should be introduced by small portions at a time, one portion being allowed to become red-hot throughout before the next is introduced. The protosulphuret is ready for use when cold. A few lumps are placed in the bottle, and covered with water, and oil of vitriol is poured in through the funnel tube. A mixture of sulphuret of antimony and hydrochloric acid may also be used for preparing sulphuretted hydrogen; but in that process the application of heat is necessary, which is not the case when protosulphuret of iron is used. For purposes of qualitative analysis, sulphuretted hydrogen may be kept in solution in water, the solution being made with distilled water, which has been

recently boiled to expel air, and preserved in carefully closed bottles, as the oxygen of the air decomposes sulphuretted hydrogen when in solution. In the absence of sulphuretted hydrogen water, and when a small quantity only of the reagent is required, it is conveniently applied by generating the gas in a test tube, moistening a piece of white paper with the solution to be tested, and holding the latter within the tube. This method is only admissible when the metal whose presence is sought affords a sulphuret of a dark colour.

16. *Hydrosulphate of ammonia*. — This useful reagent affords the means of subdividing into two groups the class of metals precipitated as sulphurets by sulphuretted hydrogen from their acid solutions, some of these sulphurets being soluble, and others insoluble, in hydrosulphate of ammonia. It is also used for subdividing into two groups the class of bases not precipitated by sulphuretted hydrogen from an acid solution; some of these bases being precipitated by hydrosulphate of ammonia, while others remain in solution. Some bases are precipitated by this reagent as oxides, and not sulphurets, merely by the action of the ammonia; this is the case, for example, with alumina and oxide of chromium, and most substances which are precipitated from their solutions by caustic ammonia, are likewise precipitated by hydrosulphate of ammonia; hence, earthy phosphates and borates, held in solution by a free acid, are precipitated by hydrosulphate of ammonia, as well as by caustic ammonia. Neutral solutions of magnesian salts, however, which afford a precipitate with caustic ammonia, give none with the hydrosulphate.

Immediately after being prepared, hydrosulphate of ammonia yields no precipitate on being mixed with a free acid; but after merely a short exposure to the air, it affords with free acids a milk-white precipitate of sulphur.*

* The composition of this reagent is represented by the formula $\text{NH}_4\text{s} + \text{Hs}$; that is, a compound of sulphuret of ammonium (NH_4s) with sulphuretted hydrogen (Hs): on exposure to the air, the hydrogen of the latter absorbs oxygen, water being thus formed, while there remains a sulphuretted sulphuret of ammonium ($\text{NH}_4\text{s} + \text{s}$) of a yellow tint, a part of the sulphur of which is precipitated on the addition of a free acid. This change of the hydrosulphate by exposure to the air does not render the reagent useless.

Hydrosulphate of ammonia is prepared by transmitting sulphuretted hydrogen gas through solution of ammonia, until the liquid gives no precipitate in a solution of sulphate of magnesia. It should be preserved in well closed bottles, which do not contain lead.

17. *Chloride of platinum.* — This reagent is used for the detection of potash, which it precipitates from tolerably strong solutions as a yellow powder, which is a double chloride of platinum and potassium. It also precipitates ammonia, but not soda. It may be prepared by dissolving metallic platinum in aqua regia, and evaporating the solution to dryness at a very moderate heat. For use, the residue may be dissolved in about eight parts of water.

18. *Phosphate of soda.* — This reagent is principally used for the detection and estimation of magnesia, which it precipitates, when ammonia is also present, as the basic phosphate of magnesia and ammonia. The removal of the other earths, if they are present, must be effected before the application of phosphate of soda, as they are likewise precipitated by this reagent, and the solution must not contain a trace of a free acid, otherwise some of the magnesia is retained in solution.

The precipitates which phosphate of soda produces in solutions of nitrate of silver and chloride of barium, should be entirely soluble in pure nitric acid; if this is not the case, some chloride or sulphate is present.

19. *Yellow prussiate of potash.* — This salt, which is met with in commerce sufficiently pure for purposes of analysis, is especially applied to the detection of copper and of iron in the state of peroxide. With the former it produces a deep reddish brown, and with the latter, a deep blue precipitate, which is one variety of prussian blue. It precipitates many other metals from their solutions; but the colours of these precipitates are not so characteristic as those with protoxide of copper, and peroxide of iron. When mixed with strong acid liquids, the prussiate of potash is subject to partial decomposition, with production of a trace of prussian blue: hence, in all minute examinations for iron, the solution, if it contains a strong acid in the free state, should be neu-

tralized or rendered alkaline by ammonia, and the excess of alkali be afterwards neutralized by a weak acid, as acetic, which may be applied in excess without inconvenience. As this reagent does not produce prussian blue with peroxide of iron in contact with a free alkali, the latter, when present, must always be neutralized by a weak acid.

20. *Red prussiate of potash.* — This reagent is employed as a test for the presence of iron in solution as protoxide. With a solution of peroxide iron it affords no characteristic appearance, but with a solution of protoxide of iron it yields a precipitate of prussian blue, similar to that produced by yellow prussiate of potash with the peroxide of iron. The presence of a free alkali prevents this indication, as in the case of the yellow prussiate.

Red prussiate of potash is best prepared by passing chlorine gas through a very dilute solution of yellow prussiate of potash, until a portion of the liquid gives no blue colour when mixed with a solution of perchloride of iron; the liquid is then concentrated by evaporation, and when near the crystallizing point, is rendered very feebly alkaline by the addition of a little carbonate of potash. The solution is filtered while hot, and allowed to cool and deposit crystals. For use, one part of these crystals should be dissolved in twenty or thirty parts of water. The solution should not afford the slightest blue tinge with a solution of perchloride of iron.

21. *Infusion of galls.* — The aqueous infusion and the alcoholic tincture of galls are employed as a test for the presence of very minute quantities of peroxide of iron in neutral solutions; the iron is precipitated as a black compound with tannic acid, which compound is the basis of common writing ink.

The infusion of galls is also used in the proximate analyses of organic substances, as a test for gelatine, which it precipitates from its solutions in brownish-white curdy flocks, which, when formed from strong solutions, cohere greatly on agitation.

The infusion of galls is conveniently prepared by digesting

for several hours one part of bruised galls in four parts of water, filtering and expressing the residue, adding two parts of common salt to the liquid, and again filtering.

22. *Chromate of potash*. — This reagent is chiefly used as a test for lead, which it precipitates from its solutions as a fine yellow powder, which is the chromate of lead, commonly called chrome-yellow.

Chromate of potash may be prepared by mixing caustic potash with an aqueous solution of the bichromate of potash of commerce, until a feebly alkaline reaction appears, and then adding a little more of the bichromate in order to restore neutrality.

This reagent occasionally contains some sulphate of potash. This is detected by the precipitate produced in the dilute solution of the chromate by nitrate of barytes not being entirely soluble in free nitric acid. Chromate of barytes is soluble, but sulphate of barytes is insoluble in nitric acid.

23. *Protochloride of tin*. — The principal applications of protochloride of tin in analysis are for the precipitation of gold and mercury from their solutions. The former is precipitated in the form of a purple powder (purple of Cassius), and the latter, provided the protochloride is applied in excess, as a grey powder consisting of metallic mercury, which runs into a globule on the application of heat. With the chloride of mercury (corrosive sublimate), the first addition of protochloride of tin produces a white precipitate of subchloride of mercury (calomel).

This reagent may be prepared by boiling granulated tin, contained in a glass retort, with concentrated hydrochloric acid, more tin being present than the acid is capable of dissolving, in order to prevent the formation of perchloride of tin. The solution is diluted with water, decanted and preserved in a well-closed bottle containing fragments of metallic tin. Its ordinary impurities are salts of iron and of lead. Hydrosulphate of ammonia should entirely redissolve the precipitate it occasions in the solution of protochloride of tin. If a black insoluble residue remains, this is either sulphuret of iron or sulphuret of lead.

24. *Chloride of lead.* — A solution of chloride of lead is conveniently used as a precipitant for silver, when lead is also present in considerable quantity. Hydrochloric acid and chloride of sodium, the ordinary precipitants of silver, also produce a precipitate with solutions of lead, except in very dilute solutions, but an aqueous solution of chloride of lead, being very weak in its strongest state, precipitates only the silver. It may be prepared by boiling litharge with hydrochloric acid, evaporating to dryness and dissolving the residue in distilled water.

25. *Sulphate of lime.* — This reagent, the saturated solution of which in water is extremely dilute, is chiefly used as a means of distinguishing between lime, strontian and barytes.

With solutions of lime, it yields no precipitate; with strontian, only after some hours; but with solutions of barytes, it yields an immediate precipitate of sulphate of barytes.

Common plaster of Paris, which has been agitated with water and well washed, may be used for preparing the aqueous solution.

26. *Antimoniate of potash.* — This substance has recently been recommended as a test for soda, which it throws down from its solution as a crystalline precipitate of slight solubility in water; but which is more freely soluble in alkaline solutions; hence the reagent should be free from an excess of alkali.

The best process for preparing antimoniate of potash seems to be the following. One part of powdered crude antimony is intimately mixed with four parts of powdered nitre, both quite dry; the mixture is projected by small portions at a time into an earthen crucible at a dull red heat, and maintained for half an hour or more in a pasty state, with occasional stirring. The mass is then cooled and washed with water until all the soluble matter present is removed and the washed residue is mixed with $\frac{2}{3}$ ths of its weight of pure carbonate of potash, and exposed to a bright red heat in an earthen crucible for half an hour. The cooled mass is digested with about fifty parts of warm water, and the solution when cold is filtered for use. Both the solution and the dry material should be preserved as much as possible from access of air.

27. *Muriate of ammonia*. — Certain bases, among which are protoxide of manganese and magnesia, which are precipitated by ammonia from their pure neutral solutions, are not thus precipitated by ammonia in the presence of an ammoniacal salt. Hence when it is an object to prevent the precipitation of such bases by ammonia, a solution of muriate of ammonia is conveniently applied for that purpose. This is, of course, unnecessary in a solution containing much free acid, as the first effect of the application of ammonia, in that case, is the formation of an ammoniacal salt. Muriate of ammonia is also used for precipitating alumina from its solution in caustic potash or soda, and for the separation of caustic lime from carbonate of lime. (See the sections which treat of the quantitative estimation of alumina and lime.)

The ordinary impurities of muriate of ammonia are sulphate of soda, sulphate of ammonia, and chloride of sodium. It should sublime without residue, and a salt of barytes should produce no precipitate in its solution. Simple recrystallization suffices to render the muriate of ammonia of commerce sufficiently pure for analytical purposes.

28. *Caustic barytes*. — Solution of caustic barytes is principally used for precipitating magnesia with a view of separating it from the fixed alkalis, and for the detection of carbonic acid. For the former purpose a solution of sulphuret of barium may be used instead of caustic barytes.

Caustic barytes may be prepared by calcining the nitrate of barytes in a porcelain crucible, at a heat approaching to whiteness, when the nitric acid of the nitrate is disengaged and caustic barytes remains. The residue is dissolved in pure water, nearly to saturation. A solution of caustic barytes may also be prepared by boiling black oxide of copper with a solution of sulphuret of barium, until a portion of the liquid, filtered, gives no black precipitate when mixed with a solution of acetate of lead. The solution is filtered while hot, diluted with water, to prevent the deposition of crystals of hydrate of barytes, and preserved in well stopped bottles. The sulphuret of barium is obtained by heating nearly to whiteness, in a covered earthen crucible, for half an hour, an intimate mixture

of eight parts of finely powdered sulphate of barytes, one part of charcoal, and two parts of flour. The mass, when cooled and digested in warm water, affords a solution of sulphuret of barium.

29. *Chloride of barium*.— This reagent is chiefly used for the detection and estimation of sulphuric acid, which it precipitates from solutions, as a white powder insoluble in all acids. Chloride of barium precipitates many other acids from neutral solutions, but the precipitates with all besides sulphuric are soluble in, or are decomposed by, hydrochloric acid.

Chloride of barium may be prepared by dissolving the native carbonate of barytes, bruised, in hydrochloric acid, evaporating to dryness, and purifying the salt by recrystallization : or, by adding a slight excess of hydrochloric acid to the solution of sulphuret of barium, made as described above, filtering the acid liquid, and evaporating it to obtain crystals. The solution, which may contain one part of the salt to twelve parts of water, should be perfectly neutral to test-paper, should not be discoloured by the addition of hydrosulphate of ammonia, and after being mixed with an excess of sulphuric acid and filtered, should leave no fixed residue on evaporation.

30. *Nitrate of barytes*.— This reagent is used for the same purposes as chloride of barium, in cases where the introduction of a chloride would not be admissible. It is obtained by digesting native carbonate of barytes in dilute nitric acid, evaporating to dryness, and purifying the salt by recrystallization. The solution should be neutral, not be rendered turbid by the addition of nitrate of silver, and should remain colourless after the addition of hydrosulphate of ammonia.

31. *Acetate of lead*.— This reagent is principally used as a test for certain acids, being employed both as a means of arranging acids into groups (some acids forming soluble and others insoluble combinations, with oxide of lead), and also for the special detection of some acids, or electro-negative constituents of salts ; particularly chromic acid, and iodine and sulphur, when combined with bases as soluble salts.

The impurities with which commercial acetate of lead is

occasionally contaminated, are acetate of lime, and acetate of iron. The whole of the lead being separated from its solution by sulphuretted hydrogen, no precipitate should be produced in the filtered solution by ammonia (*iron*), nor by oxalic acid (*lime*).

32. *Nitrate of silver*.—Oxide of silver, which is most conveniently applied, in liquid testing, in the form of nitrate of silver, affords the means of arranging acids into three distinct groups: 1. those whose combinations with oxide of silver are soluble in water, as nitric, acetic, and chloric; 2. those whose compounds with oxide of silver are insoluble in water but soluble in dilute nitric acid, as oxalic, citric, and most organic acids; and 3. those acids, or electro-negative constituents whose silver compounds are insoluble in dilute nitric acid, as chlorine, bromine, iodine, &c. Nitrate of silver is the reagent always used in quantitative analyses, for the estimation of chlorine. The solution may contain one part of the nitrate to fifteen or twenty parts of water.

To prepare pure nitrate of silver from a piece of standard silver, which contains copper, the metal is dissolved in nitric acid, the solution evaporated to dryness, and the saline residue maintained in a state of fusion in a porcelain crucible until it has lost all traces of a green colour, when the nitrate of copper will have decomposed into insoluble black oxide of copper, and nitrous vapours, which are disengaged. The residue may be dissolved in water and filtered for use, or the solution may be evaporated after filtration, in order to obtain crystals. The undissolved oxide of copper is mixed with a little silver, which may be recovered as chloride, by dissolving the powder in nitric acid, and adding common salt to the solution.

The nitrate of silver of commerce occasionally contains nitrate of copper and nitrate of potash, and is sometimes intentionally adulterated with nitrate of lead. The presence of a salt of copper is detected by the solution assuming a blue colour when mixed with an excess of ammonia. To detect nitrate of potash, the solution of the nitrate of silver is mixed with pure hydrochloric acid, in order to precipitate the whole

of the silver, filtered and evaporated: if nitrate of potash is present, a fixed residue remains after evaporation. The presence of a salt of lead is detected by adding sulphuric acid to the solution of nitrate of silver, which precipitates lead, as sulphate, if present.

33. *Ammono-nitrate of silver*.—This reagent is used for the detection of arsenic. It is prepared by adding dilute ammonia very gradually to a solution of nitrate of silver, until the oxide at first precipitate is redissolved. As an excess of ammonia would be injurious, it is advisable to leave undissolved a trace of oxide of silver, which may be separated afterwards by filtration.

34. *Iodide of potassium*.—A solution of iodide of potassium produces in solutions of certain metals precipitates of very remarkable colours, for which metals, therefore, this reagent may be employed as the test. It is principally used for the detection of lead and mercury: with salts of lead it affords a bright yellow, and with salts of the red oxide of mercury a bright scarlet compound.

The impurities with which iodide of potassium of commerce is occasionally contaminated are, carbonate of potash and alkaline chlorides. The presence of any carbonate is readily detected by the occurrence of effervescence, on the application of hydrochloric acid. To detect a chloride, the following method may be followed:—Precipitate the solution of the iodide completely by nitrate of silver, add excess of ammonia, and filter. If any chloride of silver was formed, this is now in the filtered liquid, held in solution by ammonia, and may be precipitated by nitric acid; but as iodide of silver is not perfectly insoluble in ammonia, a faint turbidity on adding nitric acid to the filtered ammoniacal solution may always be expected.

35. *Sulphate of indigo*.—A dilute solution of sulphate of indigo is employed as a test for free chlorine and free nitric acid, by both of which, when assisted by heat, its blue colour is readily destroyed.

This reagent may be prepared by digesting one part of powdered indigo in ten parts of concentrated sulphuric acid

(or what answers better, the fuming sulphuric acid) at a moderate heat, and diluting largely with water.

36. *Starch*.—Starch mucilage is used as an exceedingly delicate test for *free* iodine, with which it forms a compound of an intense blue colour. With free bromine, starch forms a yellow compound. The mucilage may be prepared by rubbing common starch with cold water, and heating the mixture nearly to the boiling point, with constant stirring. Strips cut from the elastic membrane obtained by cautiously drying a thin layer of starch mucilage have been recently recommended as a convenient form of applying starch as a test for iodine, the strips being used in the manner of test-paper.

37. *Test-papers*.—Certain vegetable colouring matters experience a remarkable change of colour when placed in contact with a free acid or alkali; which circumstance renders these bodies of great value, as reagents for the detection of free acids and alkalies. For this purpose, they may be employed in the state of aqueous infusion, or alcoholic tincture, or, what is more convenient, paper may be stained with the coloured infusion, and be wetted, when the testing is to be performed, with the liquid to be examined. Blue litmus paper is used as a test for free acids, which change the blue colour to red; and conversely, the reddened litmus paper may be used as a test for free alkalies, which restore the blue colour. The bluish-grey infusion obtained by macerating red cabbage in hot water may be used as a test both for free acids and alkalies. With the former, its colour changes to bright red, and with the latter, to bright green. The infusion of violet dahlia petals is affected in a similar manner by free acids and alkalies. Free alkalies change the yellow colour of turmeric to brown; but this effect is also produced by a few bodies which are not alkaline, among which is boracic acid. Several metallic salts, which are neutral in composition, affect test-papers in the manner of a free acid.

The most convenient test-paper is prepared by dipping good letter-paper into a concentrated infusion of the red cabbage, and drying the paper, without applying heat. The infusion should be prepared by pouring hot water upon the cabbage,

in an earthenware (not in a metallic) evaporating pan, and be concentrated by evaporation, at a temperature considerably below the boiling point. A dull grey paper is thus obtained which acquires a bright green colour by contact with alkalis, and a bright red colour by acids.

Blue litmus paper (for detecting acids) is prepared by dipping letter-paper into an infusion of litmus, made by digesting one part of powdered commercial litmus in ten parts of hot water, and filtering. If the paper reddens during desiccation, the blue colour may be restored by moistening the paper with a very dilute alkaline solution, or by very weak lime-water. For making red litmus paper (used for detecting alkalis), the infusion should be first reddened by a few drops of nitric acid.

38. *Water*. — None but distilled water is fit for general use in analytical operations. The tests of purity are nitrate of silver (for chlorides), chloride of barium (for sulphates), test-paper (for a free acid or a free alkali), oxalate of ammonia (for lime), and lime-water (for carbonic acid), neither of which should produce a turbidity in the water. A few drops, evaporated on a piece of platinum foil, should leave no stain behind. Distilled water which has been freely exposed to the air may be rendered turbid by lime-water, owing to the presence of free carbonic acid absorbed from the air, but simple ebullition suffices to expel the carbonic acid completely.

PART II.

BEHAVIOUR OF SUBSTANCES WITH REAGENTS.

DIVISION OF METALLIC BASES AND METALLIC ACIDS INTO THREE CLASSES, ACCORDING TO THEIR BEHAVIOUR WITH SULPHURETTED HYDROGEN AND HYDRO-SULPHATE OF AMMONIA.

CLASS I. Bases which are not precipitated from their solution by sulphuretted hydrogen, nor by hydrosulphate of ammonia:—

a. Alkalies; not precipitated by carbonate of soda:

| | | | |
|--------|------|--------|----------|
| Potash | Soda | Lithia | Ammonia. |
|--------|------|--------|----------|

b. Alkaline earths; precipitated by carbonate of soda:

| | | | |
|-----------|---------|----------|-------|
| Strontian | Barytes | Magnesia | Lime. |
|-----------|---------|----------|-------|

(For the behaviour of these bodies with reagents, see pp. 44—55.)

CLASS II. Metallic oxides which are precipitated by hydrosulphate of ammonia, but not by sulphuretted hydrogen (as sulphurets*) from an acid solution:—

| | | |
|--------------------|-------------------------|-----------------------|
| Alumina | Lanthanum, oxide of | Thorina |
| Cerium, oxide of | Manganese, deutoxide of | Uranium, peroxide of |
| Chromic acid | Manganese, protoxide of | Uranium, protoxide of |
| Chromium, oxide of | Manganic acid | Vanadium, oxide of |
| Cobalt, oxide of | Hyper-manganic acid | Ytria |
| Glucina | Nickel, oxide of | Zinc, oxide of |
| Iron, peroxide of | Tantallic acid | Zirconia. |
| Iron, protoxide of | Titanic acid | |

(For the behaviour of these (excepting chromic, manganic, and hyper-manganic acids) with reagents, see pp. 56—74.)

* Some of the bodies included in Class II. afford a precipitate of *sulphur* when their acid solutions are exposed to sulphuretted hydrogen, but the whole of the bases remain in solution. This precipitation of sulphur is owing to the reduction of the base from a higher to a lower degree of oxidation, by the hydrogen of the sulphuretted hydrogen, the sulphur of which is precipitated as a yellowish white powder. Solutions of the peroxide of iron and deutoxide of manganese become reduced in this way to the protoxide of iron and protoxide of manganese, with precipitation of a corresponding proportion of sulphur; the hydrogen of the sulphuretted hydrogen having united with a portion of the oxygen of the peroxide to form water.

CLASS III. Metallic oxides precipitated by sulphuretted hydrogen from acid solutions: —

a. Oxides having basic properties:

| | | |
|----------------------|-----------------------|--------------------|
| Antimony, oxide of | Lead, oxide of | Platinic oxide |
| Bismuth, oxide of | Mercury, protoxide of | Platinous oxide |
| Cadmium, oxide of | Mercury, suboxide of | Rhodic oxide |
| Copper, protoxide of | Molybdic oxide | Silver, oxide of |
| Copper, suboxide of | Molybdous oxide | Telluric oxide |
| Gold, oxide of | Osmic oxide | Tin, peroxide of |
| Iridic oxide | Palladious oxide | Tin, protoxide of. |

(For the behaviour of these with reagents, see pp. 76—99.)

b. Oxides having acid properties:

| | | |
|------------------|----------------|----------------|
| Antimonic acid | Arsenious acid | Selenious acid |
| Antimonious acid | Molybdic acid | Tungstic acid |
| Arsenic acid | Osmic acid | Vanadic acid. |

(For the behaviour of these with reagents, see pp. 100—113.)

ABBREVIATIONS AND SYMBOLS

OCCASIONALLY EMPLOYED IN THE FOLLOWING TABLES.

| | | | | | |
|-----------------|---|---|---|---|---------------------|
| am. | - | - | - | - | ammonia. |
| bicarb. | - | - | - | - | bicarbonate. |
| carb. | - | - | - | - | carbonate. |
| CO ₂ | - | - | - | - | carbonic acid. |
| conctd. | - | - | - | - | concentrated. |
| cryst. | - | - | - | - | crystalline. |
| ex. | - | - | - | - | excess. |
| gelat. | - | - | - | - | gelatinous. |
| HCl. | - | - | - | - | hydrochloric acid. |
| insol. | - | - | - | - | insoluble. |
| mur. am. | - | - | - | - | muriate of ammonia. |
| NO ₅ | - | - | - | - | nitric acid. |
| O | - | - | - | - | no precipitate. |
| pot. | - | - | - | - | potasli. |
| ppt. | - | - | - | - | precipitate. |
| ppn. | - | - | - | - | precipitation. |
| SO ₃ | - | - | - | - | sulphuric acid. |
| sol. | - | - | - | - | soluble. |
| soln. | - | - | - | - | solution. |
| solns. | - | - | - | - | solutions. |
| volum. | - | - | - | - | voluminous. |

CHAPTER I. *Behaviour of Neutral Salts of*

| <i>Alkalies.</i> | Caustic Potash. | Carbonate of Soda. | Alcoholic Solution of Chloride of Platinum. |
|----------------------------------|---|---|---|
| 1. Potash. (See also p. 48.) | | No change. | A light yellow, cryst. ppt. increased by stirring. It is insol. in HCl. |
| 2. Soda. (See also p. 49.) | No precipitate. | Ditto. | No change. |
| 3. Lithia. (See also p. 50.) | Ditto. | In concentrated solutions, after long standing a white ppt. | A faint troubling in strong solutions. |
| 4. Ammonia. (See also p. 50.) | Evolves free ammonia, which is recognised by its odour and by producing white fumes with HCl. | No precipitate. | The same appearance as with salts of potash. |

First Class of Bases with Reagents.

| Strong Solution of Tar- taric Acid. | Phosphate of Soda. | Hydrofluosilic Acid. |
|---|---|---|
| A white cryst. ppt. sol. in alkalis and acids. | No precipitate. | A very gelat. ppt. in- sol. in muriatic acid. |
| No change. | Ditto. | If the solutions are very strong, a gelat. ppt. is formed. |
| Ditto. | No ppt. But if free ammonia is added to the phosph. soda, a white ppt. falls on standing. | A white precipitate. |
| From strong solns. a white cryst. ppt. is produced. | No change. | No ppt. except in very strong solns. <i>Caus- tic</i> ammonia gives a ppt. of silicic acid. |

| <i>Earths.</i> | <i>Caustic Potash.</i> | <i>Ammonia.</i> | <i>Carbonate of Soda.</i> |
|------------------------------------|--|---|---|
| 1. Barytes. (See also p. 52.) | From a concd. soln. a white ppt. sol. in much water; the soln. becomes turbid on exposure to the air. | No ppt., but the mixture absorbs CO_2 from the air, and then deposits carb. barytes. | A white ppt. of carb. barytes. If an acid was present, the precipitation is not complete without boiling the mixture. |
| 2. Strontian. (See also p. 52.) | As barytes. | As barytes. | As barytes. |
| 3. Lime. (See also p. 53.) | Ditto. | Ditto. | Ditto. |
| 4. Magnesia. (See also p. 54.) | A white volum. ppt., sol. in mur. am. The ppt. re-appears when the soln. in mur. am. is boiled with <i>excess</i> of potash. | A white ppt. sol. in mur. am. If a salt of ammonia is present, no ppt. falls. | A bulky white ppt. sol. in mur. am. The ppt. is increased by boiling. |

ADDITIONAL OBSERVATIONS ON THE CHARACTERS OF
THE FIRST CLASS OF BASES.

The bases included in this class are distinguished from all others, by not being precipitated from their solutions either by sulphuretted hydrogen or by hydrosulphate of ammonia.

| Carbonate of Ammonia. | Oxalic Acid. | Sulphuric Acid, or Sulphate of Soda. |
|--|---|--|
| The same as with carb. soda. | No ppt. except in conctd. solns., but oxalate of ammonia gives a white ppt. | A white ppt. of sulphate of barytes, insol. in acids and alkalis. |
| As barytes. | A white ppt. if conctd.: with oxalate of ammonia, a white ppt. though the soln. is dilute. | A white ppt. of sulphate of strontian, slightly sol. in water. |
| Ditto. | A white ppt. increased on adding ammonia. Sol. in NO_3 and HCl . | A white ppt. of sulphate of lime in strong solns., sol. in much water. |
| No ppt. is produced in the cold. If the mixture is boiled a white ppt. falls, sol. in mur. am. | No ppt. except when both solns. are very strong. Oxalate of ammonia gives a white ppt. sol. in salts of am. | No change. |

The class admits of a subdivision into *alkalies*, namely, potash, soda, lithia, and ammonia; and *alkaline earths*, namely, barytes, strontian, lime, and magnesia. The basis of this subdivision is the relation of salts of the various bases to carbonate of soda or carbonate of potash, and phosphate of soda, which reagents precipitate the alkaline earths from their solutions,

but produce no change in solutions of salts of the alkalies, lithia, when in a state of strong solution, alone excepted. Lithia seems to stand midway between alkalies and alkaline earths.

General characters of alkalies.— Few compounds, comparatively, of potash, soda, and ammonia, with acids, are insoluble, or sparingly soluble in water, hence few reagents produce precipitates in solutions of salts of the alkalies. Only two reagents, namely, the antimoniate and antimonite of potash, are known, which produce a precipitate in solutions of salts of soda, of moderate strength. All salts of alkalies are colourless, except those whose acid constituents possess a colour.

Alkalies in the free and carbonated state produce a remarkable effect on certain colouring matters, so that the latter become extremely delicate tests for the presence of the former. A reddened infusion of litmus, or paper stained with the infusion, is rendered blue by these bodies. The yellow colour of paper stained with an infusion of turmeric is changed to brown by free and carbonated alkalies.

1. POTASH. — The tests generally employed to distinguish potash from the other alkalies are *tartaric acid*, and a solution of *chloride of platinum*. Before either of these tests is applied, however, the absence of ammoniacal salts should be proved, by applying caustic potash to a portion of the material, and observing whether the odour of ammonia is disengaged. If salts of ammonia are present, the material should be heated to redness, whereby all the ammonia is expelled; but the potash salt being fixed at that temperature, remains behind, and may then be dissolved in water, and tested by either of the two reagents above mentioned.

Neither chloride of platinum nor tartaric acid produces a precipitate in *dilute* solutions of potash; but in concentrated solutions, each of these reagents produces an immediate precipitate. The delicacy of these tests is considerably increased by the presence of alcohol in the mixture, the two precipitates being less soluble in alcohol than in water. The presence of a little free muriatic acid also increases the delicacy of the

chloride of platinum test : but that acid prevents the indication of tartaric acid, as it dissolves the precipitate.

The yellow precipitate produced by chloride of platinum, in solutions of potash salts, is the double chloride of platinum and potassium. The precipitate produced by tartaric acid is bitartrate of potash, or cream of tartar.

Two other reagents have been proposed as tests for distinguishing potash from the other alkalies, namely, *carbazotic acid*, and *perchloric acid*. The former produces a yellow crystalline precipitate, and the latter a white crystalline precipitate, in solutions of potash salts. Neither of these is more delicate than the two before mentioned.

Salts of potash, if free from traces of soda, communicate a faint violet tinge to the flame of alcohol. In applying this test, the salt may be moistened with water, mixed with spirits of wine, and the mixture ignited. (See also the characters of potash salts before the blowpipe.)

2. SODA.—The reagents which precipitate soda from its solutions are still fewer than those which precipitate potash. Chloride of platinum produces no precipitate in neutral soda solutions, and tartaric acid only in very concentrated. The precipitate of bitartrate of soda produced by tartaric acid is distinguished from the corresponding precipitate in potash solutions by its much greater solubility in water, and by its different crystalline form, bitartrate of soda being columnar, and bitartrate of potash granular.

The *antimoniate* and *antimonite of potash* are the only known reagents which produce a precipitate in moderately diluted solutions of salts of soda. The preparation of the antimoniate of potash is described at page 32. The precipitate of antimoniate of soda, which is granular and crystalline like the bitartrate of potash, is not deposited immediately from rather dilute solutions, being slightly soluble in water; but the deposition of the precipitate is facilitated by stirring the mixture with a glass rod. The antimoniate of soda is readily soluble in free acids; hence if a free acid is present in the solution to be tested for soda, it should be neutralized with carbonate of potash, which may be added in slight

excess, but not in large quantity, as the antimoniate of soda is more soluble in solution of carbonate of potash than in water. Other salts of potash do not interfere with the action of this test; but all ammoniacal salts do, as they are likewise precipitated by the antimoniate of potash.

Salts of soda, in very small quantity, communicate an intense yellow colour to flame. This character may be made use of as a convenient test for soda, either the flame of alcohol or the blowpipe flame being employed.

3. LITHIA. — This alkali is distinguished from potash, soda, and ammonia, 1st, by the gradual production of a precipitate of carbonate of lithia when *carbonate of soda* is added to a strong solution of a salt of lithia; 2dly, by the slow formation of a precipitate of phosphate of lithia and soda, when *phosphate of soda together with some caustic ammonia* is mixed with a strong solution of a lithia salt; and 3dly, by its property of communicating a crimson colour to flame.

If it is ascertained that the material operated on is an alkaline salt, the readiest mode of determining whether it is a salt of lithia is by its action on flame. A salt of lithia when fused on the bent end of a platinum wire, and held in the interior blowpipe flame, gives a red tinge to the exterior flame, which may last, however, only for an instant. The presence of a very small proportion of soda materially interferes with this test, when performed in the ordinary way, as the intense yellow colour produced by the soda overpowers the crimson produced by the lithia. When the experiment is conducted in the following manner, however, it is said, that lithia may be detected in a mixture of one part of chloride of lithium, and a thousand of common salt (M. Stein). The material, after being heated on the bent end of a platinum wire, in the flame of a tallow candle, is immersed in the tallow, and afterwards held in the middle of the flame. A red margin may then be perceived around the bright yellow flame of the tallow, if observed attentively.

4. AMMONIA. — The readiest and most characteristic test for ammoniacal compounds is caustic potash or soda, or

hydrate of lime, either of which disengages free ammonia from all ammoniacal salts, especially when assisted by the application of heat. The disengaged ammonia may be recognised by its peculiar and pungent odour; by its producing dense white fumes, when in contact with muriatic acid vapour (which may be applied by holding over the mixture of the material with a caustic alkali a glass rod moistened with strong hydrochloric acid); and by its action on moistened red litmus paper, the colour of which it changes to blue; but on warming the paper, the red colour reappears, owing to the volatilization of the ammonia.

Chloride of platinum and *tartaric acid* produce precipitates in solutions of ammoniacal salts, much resembling those which the same reagents produce in solutions of potash salts. The precipitate of bitartrate of ammonia produced by tartaric acid, is more soluble in water than the bitartrate of potash.

All salts of ammonia, except those having fixed acids (phosphate, borate, &c.), volatilize without residue when heated to a temperature considerably below redness. When ammoniacal salts having fixed acids are strongly heated, ammonia is disengaged and the acids remain free.

General characters of alkaline earths. — The alkaline earths, which comprise barytes, strontian, lime, and magnesia, are distinguished from alkalies, as already observed, by being precipitated from their solutions by carbonate of soda, and by phosphate of soda; which is not the case with the alkalies, lithia, when in strong solution, alone excepted. Alkaline earths are distinguished; on the other hand, from earths proper, (which form a part of Class II. p. 54.) by their solubility in water, to a greater or less extent, forming solutions which affect vegetable colours in the manner of free and carbonated alkalies; and by the solubility of their sulphurets, on which account they yield no precipitate with hydrosulphate of ammonia.

The precipitates of phosphates produced in solutions of the alkaline earths by phosphate of soda are soluble in acids, even in acetic acid.

1. **BARYTES.** — Salts of barytes are distinguished from all other substances with great ease, by the readiness with which their solutions afford a precipitate of sulphate of barytes when mixed with an extremely dilute solution of sulphuric acid or a sulphate. A *solution of sulphate of lime*, which is very weak in its strongest state, is the most convenient test for barytes, as it is not liable to confound barytes with lime and strontian, solutions of which, unless very dilute, also afford precipitates of sulphates with sulphuric acid.

Another reagent sometimes used as a test for barytes, and especially for distinguishing that earth from strontian and lime, is *hydrofluosilicic acid**, which produces in barytes solutions a crystalline precipitate of silicofluoride of barium, nearly insoluble in acids. The production of this precipitate is not immediate in dilute solutions of barytes.

2. **STRONTIAN.** — In their comportment with reagents, salts of strontian are closely related to salts of barytes, nearly all the reagents which precipitate one of these earths being capable of precipitating the other also. Owing to the slight solubility, however, of sulphate of strontian, a very weak solution of a sulphate, such as *solution of sulphate of lime*, does not produce a precipitate in strontian solutions immediately, but only after the lapse of some time. In a solution of common salt, sulphate of strontian is more freely soluble than in water.

Hydrofluosilicic acid is sometimes used to distinguish between barytes and strontian, as this reagent precipitates barytes from its solutions, but not strontian.

* A solution of hydrofluosilicic acid may be prepared by conducting into water the gaseous fluoride of silicon obtained by gently heating, in a Florence flask, a mixture of one part of powdered fluor spar, one part of siliceous sand, and six parts of oil of vitriol. The tube which conducts the gas from the flask should reach to the bottom of a glass jar, and its extremity, which should be bent upwards, is covered with mercury, in order to prevent the access of water to the tube, which would cause the latter to be choked. As the gaseous fluoride of silicon comes into contact with water, it is partially decomposed: one equivalent of fluoride of silicon (Si F_3), and three equivalents of water (3 H O), form one equivalent of silica (Si O_2), which is precipitated in a gelatinous state, and three equivalents of hydrofluoric acid (3 H F), which combines with two equivalents of unaltered fluoride of silicon, to form hydrofluosilicic acid ($3 \text{ H F} + 2 \text{ Si F}_3$).

Salts of strontian, in very minute quantity, communicate to flame a crimson colour of considerable intensity. If the material to be tested for strontian in this manner is soluble, it may be mixed with spirits of wine, and the mixture inflamed. Salts of lime also communicate to flame a red colour, but with more of a yellowish tinge than that imparted by strontian salts.

In testing for strontian a material which contains barytes, it is common to convert both these earths into dry chlorides, and treat the mixture with absolute alcohol, which dissolves chloride of strontium, but not chloride of barium.

3. LIME. — The comportment of salts of lime with the reagents mentioned in the Table, pp. 46, 47, is very similar to that of salts of barytes and strontian with the same reagents, the difference being only in intensity, according to the strength of the solutions.

The precipitate of hydrate of lime produced in solutions of salts of lime by *potash* is much less soluble in water than the corresponding precipitate of hydrate of barytes.

Owing to the solubility of sulphate of lime in water, and especially in dilute acids, *sulphuric acid* only precipitates that substance immediately from tolerably strong solutions of salts of lime. In more dilute solutions, the precipitate of sulphate of lime appears after a time, but in very dilute solutions, or, what is the same thing, when a very weak solution of a sulphate is employed, no precipitate at all appears. Sulphate of lime is still more freely soluble in a solution of common salt than in water.

The most complete precipitant of lime is *oxalate of ammonia*. This reagent, as well as *oxalic acid*, produces in neutral solutions of lime a precipitate of oxalate of lime, which is insoluble in water, oxalic acid, and acetic acid, but soluble in muriatic and nitric acids. As barytes and strontian are likewise precipitated from their solutions by oxalate of ammonia, the absence of these two earths should be insured by adding sulphate of soda to the solution to be tested, and filtering, if a precipitate is produced, before testing

for lime by oxalate of ammonia. Sufficient lime remains in solution after sulphate of soda has been applied to give a very sensible precipitate with oxalate of ammonia.

No precipitate is produced in solutions of lime by *hydrofluosilicic acid*.

Soluble salts of lime communicate a yellowish red colour to the flame of alcohol.

4. **MAGNESIA.** — Salts of magnesia are distinguishable by several characters from salts of the other alkaline earths, particularly, 1st, by the solubility of sulphate of magnesia in water, so that no precipitate is produced in magnesian solutions by *sulphuric acid*; 2dly, by the tendency of salts of magnesia to form soluble double salts with ammonia, which prevents the precipitation of magnesia *in the presence of an ammoniacal salt* by *potash, ammonia, carbonate of soda, and carbonate of ammonia* (see the Table, page 46.); and, 3dly, by the difficult solubility of the hydrate of magnesia in water, so that *ammonia* causes a precipitate of hydrate of magnesia in neutral magnesian solutions which do not contain an ammoniacal salt.

When ammonia, or carbonate of ammonia, is added to a solution of magnesia containing a free acid, an ammoniacal salt is of course formed, which prevents the precipitation of magnesia. But when either of these reagents is mixed with a *neutral* solution of a salt of magnesia, the ammoniacal salt which results from the decomposition of the magnesian salt is not in sufficient quantity to keep the whole of the magnesia present from being precipitated.

Solutions of magnesian salts are not precipitated by *hydrofluosilicic acid*.

A solution of *phosphate of soda* produces a white precipitate of phosphate of magnesia in neutral and tolerably strong solutions of magnesia. But if *ammonia* is also present, phosphate of soda is a very sensitive test for magnesia, as it precipitates that earth from very dilute solutions, as a basic phosphate of magnesia and ammonia. This precipitate is insoluble in ammoniacal salts, but freely soluble in all acids.

(For the precautions to be adopted in applying this reagent, see the process for the quantitative estimation of magnesia.)

Before testing a liquid for magnesia by phosphate of soda and ammonia, the absence of barytes, lime, and strontian should be previously secured by boiling the liquid either with carbonate of ammonia and muriate of ammonia, or with a mixture of sulphate of soda, oxalate of ammonia, and muriate of ammonia.

CHAPTER II. *Behaviour of Salts of*

| | Potash. | Carbonate of Potash. |
|---|---|---|
| 1. Alumina. (See also p. 64.) | A bulky white ppt. of hydrate of alumina, sol. in ex. ; re-pptd. by mur. am. | A bulky white ppt. (hydrate of alumina) insol. in ex., insol. in mur. am. |
| 2. Cerium, protoxide of. (See also p. 64.) | A bulky white ppt. of protoxide, insol. in ex. It becomes brownish by exposure to air. | A bulky white ppt., slightly sol. in ex. (carbonate of cerium). |
| 3. Chromium, oxide of. (See also p. 65.) | A clear green ppt. of hydrated oxide, sol. in ex., re-pptd. by mur. am. and also by long boiling. | A green ppt. of oxide of chromium becoming blue ; sol. in a large ex. |
| 4. Cobalt, oxide of. (See also p. 66.) | A blue ppt. of a subsalt of cobalt, insol. in ex. ; becomes green and red on exposure. | A red ppt. of subcarb. cobalt, which becomes blue on boiling the liquid. |
| 5. Glucina. (See also p. 66.) | A bulky white ppt. of glucina, sol. in ex. ; re-pptd. by mur. am., and also by boiling, if dilute, but not if strong. | A bulky white ppt. of carb. glucina ; sol. in large ex., insol. in mur. am. |

Second Class of Oxides with Reagents.

| Ammonia. | Carbonate of ammonia. | Hydrosulphate of Ammonia. |
|--|---|--|
| A volum. white ppt., insol. in ex.; insol. in mur. am. | As carbonate of potash. Effervescence occurs in strong solutions. | A white ppt. of hydrate of alumina, insol. in ex., sol. in potash. |
| A bulky white ppt. of protoxide, insol. in ex. | A bulky white ppt. of carbonate of cerium, slightly sol. in ex. | A white ppt. of protoxide. |
| A greenish ppt. of hydrated oxide, slightly sol. in ex., if cold, but not if hot. | A green ppt. of hydrated oxide, containing a little carbonate. | A greenish ppt. of oxide of chromium, with a little sulphuret, insol. in excess. |
| First a blue ppt. of subsalt; on adding more am. it becomes green; sol. in large ex.; sol. in mur. am. | In neutral solutions, a red ppt. of carbonate, sol. in mur. am. | A black ppt., insol. in ex., and in alkalies (sulphuret). |
| A bulky white ppt. of glucina, insol. in ex. and in mur. am. | A bulky white ppt. of carb. glucina, sol. in ex. | A white ppt., sol. in potash (glucina). |

| | Potash. | Carbonate of Potash. |
|---|--|--|
| 6. Iron, peroxide of. (See also p. 67.) | A brownish red ppt. of hydrated peroxide, insol. in ex. | The same as potash. Effervescence of CO_2 in strong solutions. |
| 7. Iron, protoxide of. (See also p. 68.) | First a white ppt. of hydrated protoxide, which becomes green, and, lastly, brown, by exposure to air. | A greenish-white ppt. of carbonate, which becomes greener, and afterwards red by exposure to air. No ppt. if salts of am. are present. |
| 8. Lanthanum, oxide of. (See also p. 68.) | A reddish white ppt. of hydrated oxide, insol. in ex. | A bulky white ppt. of carbonate, insol. in ex. |
| 9. Manganese, protoxide of. (See also p. 69.) | A white ppt. of protoxide, rather sol. in mur. am. By exposure to air the ppt. absorbs oxygen and becomes brown. | A white ppt. of carbonate, which does not blacken unless ignited: slightly sol. in mur. am. |
| 10. Manganese, deutoxide of. (See also p. 69.) | A bulky brown ppt. of hydrated deutoxide, insol. in mur. am. | The same as potash. |
| 11. Nickel, oxide of. (See also p. 70.) | An apple-green ppt. of oxide, insol. in ex., sol. in carbonate of ammonia. | An apple-green ppt. of carbonate of nickel. |

| Ammonia. | Carbonate of Ammonia. | Hydrosulphate of Ammonia. |
|--|--|--|
| The same as potash. | As potash. The ppt. is partially sol. in excess, unless the soln. is dilute. | A black ppt., insol. in ex. and in alkalies; sol. in HCl. and NO_3 , becomes brown on exposure (proto-sulphuret). |
| The same as potash. No ppt. if ammoniacal salts are present. | The same as carbonate of potash. | Ditto. |
| A bulky white ppt. of a subsalt, insol. in ex., insol. in mur. am. | The same as carbonate of potash. | A white ppt. (oxide). |
| A white ppt. of protoxide, which blackens on exposure; mur. am. prevents this precipitation. | The same as carbonate of potash. | Flesh colour, insol. in ex. and in alkalies, blackens on exposure (sulphuret). |
| As potash. | As potash. | Flesh colour, insol. in ex. (sulphuret). |
| A green ppt. of oxide, sol. in ex.; re-precipitated by potash. | In neutral but not in acid solutions an apple green ppt., sol. in ex. | A black ppt., slightly sol. in ex. (sulphuret). |

| | Potash. | Carbonate of Potash. |
|--|---|--|
| 12. <i>Tantalic acid</i> . (Solution in bin- oxalate of pot- ash.) (See also p. 70.) | A white ppt. sol. in large ex. | A white ppt. |
| 13. <i>Titanic acid</i> . (Solution of al- kaline titanate in a small quan- tity of HCl.) (See also p. 70.) | A white ppt. of titanic acid, insol. in ex., sol. in mur. acid. | A white ppt. of titanic acid, slightly sol. in ex., sol. in HCl. |
| 14. <i>Thorina</i> . (See also p. 71.) | A gelatinous white ppt. of thorina, insol. in ex. | A white ppt. of sub- carbonate, sol. in large ex. |
| 15. <i>Uranium, prot- oxide of</i> . (See also p. 71.) | A bulky brown ppt. of oxide, insol. in ex. | A greenish ppt. of carbonate, sol. in large ex. |
| 16. <i>Uranium, per- oxide of</i> . (See also p. 72.) | A yellow ppt. of ura- nate of pot., insol. in ex. | A yellow ppt., sol. in ex.; re-pptd. on standing. |
| 17. <i>Vanadium, ox- ide of</i> . (See also p. 72.) | A dirty white ppt. of hydrated oxide, sol. in ex.; re-pptd. by a greater ex. in com- bination with pot. | The same as potash. |
| 18. <i>Yttria</i> . (See also p. 73.) | A volum. white ppt. of hydrate of yttria, insol. in ex. | A bulky white ppt. of carbonate, slightly sol. in ex. |

| Ammonia. | Carbonate of Ammonia. | Hydrosulphate of Ammonia. |
|---|--|--|
| A white ppt., insol. in ex. | A white ppt. insol. in ex. | A white ppt. with effervescence (tantalalic acid). |
| The same as potash. | The same as carbonate of potash. | A white ppt. of titanic acid. |
| The same as potash. | The same as carbonate of potash. | A white ppt. of thorina. |
| A dark brown ppt. of oxide, insol. in ex.; becomes yellow on exposure to air. | A greenish ppt. of carbonate, sol. in ex. | A black ppt., insol. in ex. (proto-sulphuret). |
| A yellow ppt. of uranate of ammonia, insol. in ex. | The same as carbonate of potash. | Brown, very slightly sol. in ex. (persulphuret). |
| A brown ppt., sol. in pure water, but insol. in water containing ammonia. | A grey ppt. gradually becoming brown. | Brown black, sol. in ex., forming a purple solution (sulphuret). |
| A bulky white ppt. of hydrate of yttria, insol. in ex. | A bulky white ppt. of carbonate, sol. in large ex. | A white ppt. of hydrate of yttria. |

| | Potash. | Carbonate of Potash. |
|--|---|---|
| 19. Zirconia. (See also p. 73.) | A bulky white ppt. of hydrate of zirconia, insoluble in ex. | No ppt. at first; afterwards a bulky white ppt. of carbonate, slightly sol. in ex. |
| 20. Zinc, oxide of. (See also p. 73.) | A gelat. white ppt. of hydrated oxide, sol. in ex, | A white ppt. of sub-carbonate, insol. in ex.; sol. in potash, am. and ammoniacal salts. |

ADDITIONAL OBSERVATIONS ON THE CHARACTERS OF
THE SECOND CLASS OF METALLIC OXIDES.

The bodies included in this class are distinguished from all other substances by their comportment with sulphuretted hydrogen and hydrosulphate of ammonia. Unlike the members of the *First Class* (pp. 44, 45.), they are precipitated by hydrosulphate of ammonia; and they differ from the *Third Class* in not being precipitated from solutions containing a free acid, by sulphuretted hydrogen. In some other respects the members of this class exhibit considerable dissimilarity in their comportment with reagents.

Of the hydrated oxides precipitated by caustic potash from solutions of these bodies, some are easily and completely dissolved by an excess of the alkali, but others remain undissolved. Those which are soluble in solution of potash are,

Alumina,
Oxide of chromium,
Glucina.
Tantallic acid (hydrated),
Oxide of vanadium,
Oxide of zinc.

The precipitates produced in the neutral solutions of these bodies by hydrosulphate of ammonia do not all possess a

| Ammonia. | Carbonate of Ammonia. | Hydrosulphate of Ammonia. |
|---|--|--|
| The same as potash. | A bulky white ppt. of carbonate, sol. in ex. | A bulky white ppt. of zirconia. |
| A bulky white ppt. of hydrated oxide, sol. in ex. | A white ppt. of sub-carbonate, sol. in ex. | A white ppt., insol. in ex. (sulphuret). |

similar chemical constitution, some of these precipitates being hydrated oxides, while others are sulphurets. The following are those whose solutions afford precipitates of hydrated oxides with hydrosulphate of ammonia :—

Alumina,
Protoxide of cerium,
Oxide of chromium,
Glucina,
Oxide of lanthanum,
Tantalac acid,
Titanic acid,
Thorina,
Yttria,
Zirconia.

The precipitates produced by hydrosulphate of ammonia in solutions of the following are sulphurets :—

Oxide of cobalt,
Peroxide of iron,
Protoxide of iron,
Protoxide of manganese,
Deutoxide of manganese,
Oxide of nickel,
Protoxide of uranium,
Peroxide of uranium,
Oxide of vanadium,
Oxide of zinc.

1. *Alumina*. — The soluble salts of alumina, though neutral in constitution, affect litmus paper in the manner of free acids, and possess an astringent and slightly acid taste. Pure alumina is perfectly insoluble in water.

A strong solution of an aluminous salt, when mixed with a saturated solution of *sulphate of potash and a little free sulphuric acid* affords crystals of common alum.

Alumina is recognised by its solubility in potash, insolubility in ammonia and alkaline carbonates, and freedom from colour. A characteristic test for this earth consists in heating it before the blowpipe with a solution of nitrate of cobalt, whereby it requires an azure colour (see the chapter on Blowpipe Analysis).

The action of reagents on solutions of alumina is greatly impeded by the presence of non-volatile organic matters, that is, those organic bodies not volatilized by heat without being carbonized. When these are present, the solution should be evaporated to dryness, the organic matters destroyed by calcination at a red heat, and the residue be dissolved in hydrochloric acid; to which solution the tests for alumina should be applied.

2. *Protoxide of cerium*. — The neutral salts of protoxide of cerium redden litmus paper in the manner of free acids. The white hydrated protoxide of cerium, as precipitated by caustic alkalis from solutions of the protoxide, becomes brownish when exposed to the air, through the absorption of oxygen, the protoxide of cerium being converted into the peroxide. By calcination in the open air the protoxide acquires a reddish colour through the absorption of oxygen. This is one of the tests employed to distinguish protoxide of cerium from thorina and yttria.

When a very dilute solution of sulphate of protoxide of cerium (say one part of the sulphate in one hundred parts or more of water) is boiled, the liquid becomes opaque, and deposits a yellow precipitate of subsulphate of protoxide of cerium. By this character, protoxide of cerium may be distinguished from oxide of lanthanum.

From alumina and glucina, protoxide of cerium differs by its insolubility in caustic potash. The presence of non-volatile organic matters prevents the precipitation of protoxide of cerium by alkalies.

The *peroxide of cerium* dissolves in hot hydrochloric acid, with disengagement of chlorine, and reduction of the peroxide to protoxide of cerium. Even when the peroxide of cerium is dissolved in dilute boiling sulphuric acid, the peroxide is likewise reduced to protoxide. The precipitates of protoxide of cerium, however, produced by alkalies in such solutions, have a yellowish tint, due to the presence of a little peroxide (Rose). Valerianic acid, according to M. Buonaparte, precipitates peroxide of cerium from its solutions.

3. *Oxide of chromium*. — The solutions of most of the salts of oxide of chromium possess a green colour by reflected, and a reddish violet colour by transmitted, light. The soluble neutral salts of chromium redden litmus paper. Before being ignited, oxide of chromium is readily dissolved by acids, but afterwards it is insoluble in all acids with the exception of hot concentrated sulphuric acid.

When oxide of chromium or any compound containing that oxide is fused with nitre, the oxide of chromium acquires oxygen, and passes into the state of chromic acid, which unites with the potash of the nitre to form the yellow chromate of potash. This compound forms a deep yellow solution in water. (See the characters of chromic acid.)

The blowpipe tests for oxide of chromium are particularly delicate. (See the chapter on Blowpipe Analysis.)

Oxide of chromium approaches very near to alumina in its comportment with reagents, both these bases being soluble in a caustic alkali, and capable of being reprecipitated from such a solution by muriate of ammonia; on which account alumina may sometimes be overlooked, when mixed with oxide of chromium. The solubility of the oxide of chromium in a large excess of a solution of carbonate of potash presents one mode of separating these two bases; and the

precipitability of oxide of chromium from its solution in caustic potash by ebullition affords another mode. The best method, however, consists in fusing the mixture with nitre, in order to convert the oxide of chromium into chromic acid, and adding muriate of ammonia to the solution of the fused mass in water, whereupon alumina, if present, is precipitated.

The presence of non-volatile organic bodies impedes the precipitation of oxide of chromium by the alkalis.

4. *Oxide of cobalt.* — Solutions of oxide of cobalt, and most hydrated salts of this oxide, possess a peculiar reddish colour; but the anhydrous compounds of oxide of cobalt are mostly blue. The precipitation of oxide of cobalt by alkalis, but not by hydrosulphate of ammonia, is impeded by the presence of non-volatile organic bodies. The soluble salts of cobalt redden litmus paper, though neutral in constitution. In strong *acid* solutions of cobalt, *ammonia* produces no precipitate, because the ammoniacal salt produced by ammonia and the free acid retains the oxide of cobalt in solution. Hydrosulphate of ammonia, however, precipitates all the cobalt from such an ammoniacal solution, as sulphuret.

By far the most delicate, as well as characteristic, test for cobalt consists in fusing the substance with borax before the blowpipe, as the smallest trace of cobalt communicates to melted borax a decided blue colour. (See the chapter on Blowpipe Analysis.)

5. *Glucina.* — When hot solutions of salts of glucina are mixed with a hot solution of *fluoride of potassium* until a precipitate begins to appear, on cooling the mixture, a slightly soluble double fluoride of glucinum and potassium is deposited in scaly crystals. According to Berzelius, this property is characteristic of salts of glucina. It must be remembered, however, that oxide of lanthanum produces a white flocculent precipitate with fluoride of sodium.

Neutral solutions of salts of glucina redden litmus paper, and possess a rather characteristic sweet taste. The usual

action of reagents on solutions of glucina is impeded by the presence of non-volatile organic matters; these bodies should therefore be destroyed by ignition, and the residue be dissolved in hydrochloric acid.

The solubility of glucina in caustic potash may sometimes lead to the confusion of this earth with alumina. These bodies are distinguished by the solubility of glucina in alkaline carbonates, particularly carbonate of ammonia, and by the different appearances they present when heated with a solution of nitrate of cobalt before the blowpipe. (See the chapter on Blowpipe Analysis.)

6. *Peroxide of iron*.—The usual colour of strong solutions of peroxide of iron is reddish or yellow. Blue litmus paper is reddened by neutral solutions of the peroxide of iron.

An extremely delicate and characteristic test for peroxide of iron in neutral or slightly acid solutions is the *yellow prussiate of potash*, which produces a deep blue precipitate of prussian blue, insoluble in acids, but decomposed by caustic alkalis, with separation of peroxide of iron. (See page 29.)

A solution of *red prussiate of potash* imparts a brownish green colour to solutions of peroxide of iron, but no precipitate is formed.

In neutral and acid solutions of peroxide of iron, *sulphuretted hydrogen* causes a milk-white precipitate of sulphur, and reduces the peroxide to the state of protoxide, or the perchloride to protochloride (see the note at page 41.); but all the iron remains in solution.

A very delicate test for peroxide of iron is an *infusion of gall-nuts*, which produces a blueish-black precipitate, in solutions of this oxide containing no free acid or alkali, and no oxidizing agent, such as free chlorine. (See page 30.)

In the presence of non-volatile organic bodies, peroxide of iron is not precipitated by alkalis; these matters, however, do not hinder its detection by yellow prussiate of potash.

When a solution containing peroxide of iron is heated with

any non-volatile polybasic * acid (as tartaric, citric, racemic, malic, mucic, and kinic acids), or in fact with most common vegetable matters, as chips of wood, twigs of trees, hay, sugar, starch, paper, &c., the peroxide of iron is reduced to protoxide with facility. In some cases the reduction takes place at the ordinary temperature.

7. *Protoxide of iron.* — The hydrated salts of protoxide of iron and their strong solutions possess a greenish colour. Litmus paper is reddened by the soluble neutral salts of this oxide.

The *red prussiate of potash* is as delicate and characteristic a test for protoxide of iron, as the yellow prussiate of potash is for the peroxide. With extremely minute traces of protoxide of iron, the red prussiate produces a deep blue precipitate, consisting of a variety of prussian blue, which is insoluble in acids, but is decomposed by caustic alkalies with separation of protoxide of iron. (See page 30.)

The *yellow prussiate of potash* produces in a solution of protoxide of iron, perfectly free from the peroxide, a greenish white precipitate, which soon absorbs oxygen from the air and becomes blue.

The presence of ammoniacal salts partially prevents the precipitation of protoxide of iron by *caustic potash*, and entirely by *ammonia*, but not by *hydrosulphate of ammonia*. Several organic matters likewise impede the precipitation of protoxide of iron by alkalies.

Protoxide of iron in solution may be distinguished from all other metallic oxides by its comportment with the red prussiate of potash described above.

8. *Oxide of lanthanum.* — The hydrated salts of oxide of lanthanum, according to M. Hermann, mostly possess a rose colour. *Fluoride of sodium* produces in their solutions a white flocculent precipitate of fluoride of lanthanum; *sulphate of potash*, a white pulverulent precipitate of double sulphate

* By a polybasic acid is meant an acid, one equivalent of which requires more than one equivalent of a base to form a neutral salt.

of oxide of lanthanum and potash of difficult solubility ; *phosphoric and oxalic acids and their salts*, white precipitates slightly soluble in an excess of the acid ; and *yellow prussiate of potash*, a white precipitate.

The reddish brown precipitate of hydrated oxide of lanthanum produced by caustic potash speedily absorbs carbonic acid when exposed to the air, and thereby becomes white, if free from oxide of cerium and protoxide of manganese. When ammonia is added to a solution of oxide of lanthanum, also containing an earth or a metallic oxide, which is not commonly precipitated by ammonia in the presence of an ammoniacal salt, as lime, magnesia, and protoxide of manganese, the subsalt of lanthanum thereupon precipitated always carries down with it a portion of the other base present, whatever quantity of an ammoniacal salt be applied to retain the other bases in solution (M. Hermann).

9. *Protoxide of manganese*.—The hydrated salts of protoxide of manganese and their strong solutions possess a faint pink colour. Their neutral solutions do not affect litmus paper.

The presence of ammoniacal salts in considerable quantity partially prevents the precipitation of protoxide of manganese by *caustic potash*, and completely by *caustic ammonia*, a double salt of protoxide of manganese and ammonia being formed, which resists decomposition by ammonia. When a solution of such a double salt containing free ammonia is exposed to the air, oxygen is gradually absorbed, and a brown precipitate of hydrated peroxide of manganese is formed.

A solution of *chloride of lime* (bleaching powder) produces in solutions of protoxide of manganese, a brown precipitate of hydrated peroxide of manganese. (See the chapter on Blowpipe Analysis for an extremely delicate and characteristic test for manganese.)

10. *Deutoxide of manganese*.—The deutoxide of manganese dissolves in cold hydrochloric acid, forming a deep brown

solution, and in cold sulphuric acid, a little diluted, forming a violet coloured liquid. Both of these solutions, however, are converted by ebullition into solutions of the protoxide of manganese; rapidly in the case of hydrochloric acid, with evolution of free chlorine; but slowly in the case of sulphuric acid, with disengagement of oxygen. Deutoxide of manganese, in solution, is readily reduced to protoxide by contact with organic matters.

Sulphuretted hydrogen produces in solutions of the deutoxide of manganese, a milk-white precipitate of sulphur, through the reduction of the deutoxide to protoxide. (See the note at page 41.)

11. *Oxide of nickel*.—The hydrated salts of nickel and their solutions possess a green colour, and redden litmus paper freely.

In qualitative analysis, oxide of nickel is sometimes confounded with oxide of cobalt. These oxides may be distinguished by the comportment of their ammoniacal solutions with caustic potash. The ammoniacal solution of oxide of cobalt, if it contains a small quantity of a salt of ammonia, does not afford a precipitate with caustic potash; but the ammoniacal solution of oxide of nickel yields in such circumstances a precipitate of oxide of nickel. (See also a process for the quantitative separation of cobalt from nickel, by means of cyanide of potassium.)

The presence of organic bodies impedes the precipitation of oxide of nickel by alkalies, but not by hydrosulphate of ammonia. (See the Blowpipe Test for Nickel.)

12. *Tantallic acid*.—After having been heated to redness, alone, tantallic acid is insoluble in all liquids. After having been fused with potash, it dissolves in water, and in this alkaline solution hydrochloric acid produces a precipitate of tantallic acid, which is insoluble in an excess of acid. According to Rose, this is the most characteristic property of tantallic acid.

From silica, with which it might be confounded by the

above test, tantalic acid is distinguished by its characters before the blow-pipe. (See the chapter on Blowpipe Analysis.)

13. *Titanic acid*.—After having been heated to redness, alone, titanic acid is insoluble in all acids with the exception of boiling oil of vitriol. The precipitate of titanic acid produced by adding ammonia, to a solution of an alkaline titanate in hydrochloric acid, is soluble in hydrochloric acid, unless it has been warmed even slightly, in which case it does not form a clear solution. (Rose.)

When the solution of an alkaline titanate in hydrochloric acid is boiled, titanic acid is precipitated (though incompletely) in a form nearly insoluble in acids. The precipitation of titanic acid by ebullition is more complete when the solution of the acid has been effected in concentrated sulphuric acid, and the solution afterwards largely diluted.

When a piece of metallic zinc is placed in a solution of an alkaline titanate in hydrochloric acid, the liquid gradually acquires a blue colour, and at length a blue precipitate is formed, which slowly becomes white. If the zinc is removed from the blue liquid while the latter is yet clear, and caustic potash or ammonia applied, a blue precipitate is produced, which gradually whitens, with disengagement of hydrogen gas. If the titanic acid has been previously precipitated by ebullition, it likewise becomes blue by contact with zinc. A very dilute solution of titanic acid does not, however, afford these indications. A piece of tin or iron may be substituted for zinc in this experiment. (Rose.)

The presence of several non-volatile vegetable matters prevents the precipitation of titanic acid by the alkalies, and also by ebullition.

Titanic acid may be distinguished from all other bodies by its property of being precipitated by ebullition, and by its comportment with metallic zinc.

14. *Thorina*.—The salts of thorina, which are soluble in water, are decomposed by being heated to redness, their acids

being volatilised. The solutions of the sulphate, and some other salts of this earth, afford precipitates on being boiled; except when a base is present, with which thorina forms a double salt, in which case no change occurs on ebullition. Thorina is distinguished from alumina and glucina by being insoluble in caustic potash.

15. *Protoxide of uranium*.—The compounds of protoxide of uranium generally possess a green colour. Pure protoxide of uranium is scarcely soluble in hydrochloric acid; but in sulphuric acid, slightly diluted, it dissolves with the aid of heat, forming a green solution. It readily dissolves in nitric acid, but not without conversion into the peroxide of uranium.

Non-volatile organic matters prevent the precipitation of protoxide of uranium by alkalies.

As the indications of protoxide of uranium with re-agents are not so characteristic as those of peroxide of uranium, it is advisable, when testing for uranium, to heat the substance with nitric acid, in order to convert the protoxide, if present, into peroxide.

16. *Peroxide of uranium*.—Most of the compounds containing peroxide of uranium, whether soluble or insoluble, possess a yellow colour. The yellow precipitates produced in solutions of the peroxide of uranium by alkalies are combinations of the alkali with the peroxide, and not the hydrated peroxide itself. When the precipitate produced by ammonia is heated to redness, ammonia and oxygen gas are disengaged, and the dark green protoxide of uranium remains, insoluble in hydrochloric acid. But if the peroxide of uranium is associated with a fixed alkaline, or an earthy base, it does not become reduced to the protoxide by calcination.

Almost all the compounds of peroxide of uranium, which are insoluble in water, are soluble in hydrochloric acid. The acids contained in such insoluble compounds are best

separated from the peroxide of uranium by hydrosulphate of ammonia. (See such a process as this for the quantitative separation of phosphoric acid from peroxide of uranium, under Phosphorus.)

Peroxide of uranium is distinguished from other bodies by its comportment with alkalies and hydrosulphate of ammonia. The appearances which oxide of uranium presents before the blowpipe are also characteristic.

Non-volatile organic bodies impede the precipitation of peroxide of uranium by alkalies to a certain extent.

17. *Oxide of vanadium*.—The aqueous solutions of salts of vanadium possess a fine blue colour, but of little depth. Their taste is sweetish and astringent, like that of the salts of protoxide of iron. Oxide of vanadium is soluble in acids after being ignited, though but slowly.

Vanadium is most easily recognised by re-agents when in the state of vanadic acid (the characters of which are described at pp. 102. 112.); hence it is advisable to fuse the substance under examination with nitre, in order to convert the lower oxides of vanadium, if present, into vanadic acid, and to apply the tests for vanadic acid to the solution of the fused mass.

18. *Yttria*.—The neutral salts of yttria redden litmus paper, and possess a sweetish astringent taste. Yttria, unlike zirconia, is soluble in acids after being calcined.

Yttria is distinguished from several of the earths with which it is likely to be confounded, by *oxalic acid*, which produces even in slightly acid solutions of yttria a voluminous white precipitate of oxalate of yttria, soluble in hydrochloric acid.

From alumina and glucina, yttria is distinguished by its insolubility in caustic potash.

19. *Zirconia*.—The neutral solutions of salts of zirconia redden litmus paper. In the hydrated state, zirconia is

easy of solution in acids, but, after being strongly heated, it is insoluble in nearly all acids. This character serves to distinguish zirconia from yttria. Boiling sulphuric acid, however, slowly acts on ignited zirconia, and renders it soluble in water.

Oxalic acid produces in solutions of zirconia a bulky precipitate of oxalate of zirconia, which is soluble only in a large excess of hydrochloric acid.

A solution of *sulphite of ammonia* produces, in neutral solutions of zirconia, a precipitate of subsulphite of zirconia, which dissolves on applying an excess of sulphite of ammonia. On boiling this solution, sulphurous acid is disengaged, and hydrate of zirconia is precipitated.

Several organic substances and an *excess* of sulphite of ammonia prevent the precipitation of zirconia by alkalies.

20. *Oxide of zinc*.—The compounds of oxide of zinc are colourless, except those which derive a colour from their constituent acid. Their neutral solutions redden litmus paper. Strong ignition does not render oxide of zinc insoluble in acids.

Sulphuretted hydrogen produces a white precipitate of sulphuret of zinc in neutral, but not in acid, solutions of zinc. If, however, the free acid be a weak one, as acetic, sulphuretted hydrogen may produce a precipitate of sulphuret. Hydrosulphate of ammonia precipitates sulphuret of zinc from neutral and alkaline solutions of oxide of zinc.

The action of re-agents on solutions of zinc is considerably interfered with by the presence of non-volatile organic matters. To detect zinc in a solution containing such bodies, ammonia in excess may be added to the solution, and if a precipitate is produced, the liquid should be filtered, and the precipitate examined for zinc before the blowpipe. The filtered liquid should also be tested for zinc by hydrosulphate of ammonia, and the precipitate thereby produced, if there is any, should be examined before the blowpipe. It is sometimes necessary to decompose the organic matters by boiling the substance with dilute nitric acid, then to filter and test the filtered

liquid with ammonia and hydrosulphate of ammonia, as above.

The comportment of oxide of zinc when heated alone on charcoal before the blowpipe, and also with a solution of nitrate of cobalt, is characteristic. (See the chapter on Blowpipe Analysis.)

The principal characters by which oxide of zinc may be recognised are its solubility in potash and ammonia, and its precipitability from alkaline as well as neutral solutions by hydrosulphate of ammonia, as a white sulphuret.

CHAPTER III.—*Behaviour of Salts of*

SECTION I.

| | Potash. | Carbonate of Potash. | Ammonia. |
|---|---|---|---|
| 1. Antimony, oxide of. (Solution in hydrochloric acid.) (See also p. 85.) | A white ppt. of oxide, sol. in ex. | A white ppt. of oxide, insol. in ex. | A white ppt. of oxide, insol. in ex. |
| 2. Bismuth, oxide of. (See also p. 85.) | A white ppt. of oxide, insol. in ex. | A white ppt. of carbonate, insol. in ex. | A white ppt. of oxide, insol. in ex. |
| 3. Cadmium, oxide of. (See also p. 86.) | A white ppt. of oxide, insol. in ex. | A white ppt. of carbonate, insol. in ex. | A white ppt. of oxide, very sol. in ex. |
| 4. Copper, suboxide of. (See also p. 87.) | Pot. in ex. produces a yellowish ppt. of suboxide, which becomes black on exposure. | A yellow ppt. of carbonate of suboxide of copper. | Excess of am. forms a colourless liquid, which becomes blue on exposure to air, through the absorption of oxygen. |

*Third Class of Oxides with Re-agents.***BASES.**

| Carbonate of Ammonia. | Hydrosulphate of Ammonia. | Sulphuretted Hydrogen (in an acid liquid). |
|---|---|--|
| A white ppt. of oxide, insol. in ex. | An orange red ppt. of sulphuret, sol. in ex. ; reprecipitated by acids. | An orange red ppt. of sulphuret, in acid solns., sol. in alkaline sulphurets, in potash, and in boiling HCl. |
| A white ppt. of carbonate, insol. in ex. ; effervescence. | A black ppt. of sulphuret, insol. in alkaline sulphurets, alkalies, and dilute acids. | A black ppt. of sulphuret, insol. in alkalies, alkaline sulphurets, and dilute acids. |
| A white ppt. of carbonate, insol. in ex., and in mur. am. | A yellow ppt. of sulphuret, insol. in ex. | A yellow ppt. of sulphuret, insol. in alkalies, and alkaline sulphurets. |
| The same as ammonia. | A black ppt. of subsulphuret, insol. in ex. | A black or brown ppt. of subsulphuret, insoluble in alkaline sulphurets. |

| | Potash. | Carbonate of Potash. | Ammonia. |
|---|--|--|--|
| 5. Copper, protoxide of. (See also p. 87.) | A blue ppt. of hydrated oxide, insol. in ex.; it becomes black, and anhydrous on being heated. | A blue ppt. of carbonate; it becomes black on being heated. | A blue ppt. of sub-salt, very sol. in ex., giving a deep blue solution, reprecipitated by excess of potash as oxide. |
| 6. Gold, perchloride of. (See also p. 89.) | In strong solns. only, a slight reddish ppt., sol. in ex. (peroxide of gold). | No precipitate. | In strong solns. only, a yellow ppt. (fulminating gold). |
| 7. Iridic oxide. (See also p. 90.) | By pot. in ex. the soln. is decolorised; only a very slight brown ppt. falls. On standing, the mixture becomes blue. | A brown red ppt. which slowly dissolves in an ex. | As potash. When the mixture is exposed to the air, a slight blue ppt. falls. |
| 8. Lead, oxide of. (See also p. 91.) | A white ppt., sol. in large ex. (as subsalt). | A white ppt. of carbonate, insol. in ex., sol. in potash. | A white ppt. of a sub-salt, insol. in ex. (slowly formed in acetate). |
| 9. Mercury, suboxide of. (See also p. 91.) | A black ppt. of protoxide, insol. in ex. | A yellow ppt. of carbonate, which becomes black on being heated. | A black ppt., insol. in ex. (a basic salt of suboxide and am.) |

| Carbonate of Ammonia. | Hydrosulphate of Ammonia. | Sulphuretted Hydrogen. (in an acid liquid). |
|--|--|--|
| The same as ammonia. | The same as sulphuretted hydrogen. | Brownish black sulphuret, insol. in alkalies, dilute acids, and sulphuret of potassium. |
| In strong solns., a yellow ppt. with effervescence (fulminating gold). | A dark brown ppt. of sulphuret of gold, sol. in ex. | A black ppt. of sulphuret. |
| No ppt., but the soln. is slowly decolorised. | A brown ppt. of sulphuret, sol. in ex. | The liquid is first decolorised, afterwards a brown ppt. is slowly formed. |
| A white ppt. of carbonate, insol. in ex.; sol. in potash. | A black ppt. of sulphuret, insol. in ex., in alkalies and dilute acids; it is decomposed by boiling nitric acid. | A black ppt. of sulphuret, insol. in alkalies, alkaline sulphurets, and dilute acids. |
| Carb. am. in small quantity gives a grey ppt.; in a large quantity, a black one. | A black subsulphuret, insol. in ex.; resolved by pot. into metallic mercury and bisulphuret. | Black sulphuret, insol. in NO_5 , and alkaline sulphurets; sol. with decomposition in aqua regia. |

| | Potash. | Carbonate of Potash. | Ammonia. |
|---|--|--|--|
| 10. Mercury, protoxide of. (See also p. 92.) | Pot. in excess gives a yellow ppt. of protoxide, insol. in ex.; but if mur. am. is present, a white ppt. | A reddish brown ppt.; or if mur. am. is present, a white ppt. | A white ppt., insol. in ex. (a basic salt of protoxide and am.). |
| 11. Molybdous oxide. (See also p. 94.) | A brown black ppt., insol. in ex. (hydrate of the oxide). | A brown black ppt., slightly sol. in ex. (hydrate of the oxide). | A brown black ppt., insol. in ex. (hydrate of the oxide). |
| 12. Molybdic oxide. (See also p. 94.) | A bulky brown black ppt., insol. in ex. (hydrated oxide). | A brown ppt., sol. in ex. (hydrated oxide). | A bulky brown black ppt., insol. in ex. (hydrated oxide). |
| 13. Osmic oxide. (See also p. 95.) | A black ppt. formed only on boiling, or after standing some time. | A black ppt. on standing. The liquor above is bluish. | A brown ppt. falls after some time. |
| 14. Palladium oxide. (See also p. 95.) | A yellowish brown ppt., sol. in ex. (a sub-salt). | A brownish ppt. of hydrated oxide, sol. in ex., reprecipitated on boiling. | A yellowish brown ppt., sol. in ex. (a sub-salt). |
| 15. Platinous oxide. (See also p. 95.) | No ppt., if quite free from platinic oxide. | A brown ppt., slowly formed. | A green, crystalline ppt. of a double salt, containing am. |

| Carbonate of Ammonia. | Hydrosulphate of Ammonia. | Sulphuretted Hydrogen (in an acid liquid). |
|---|---|--|
| A white ppt. of a basic salt of protoxide and ammonia. | If in ex. a brown ppt. of protosulphuret, insol. in ex. (see page 93.). | If in excess, a brown ppt. (see page 93.). |
| A brown black ppt., sol. in ex. (hydrate of the oxide). | A yellowish brown ppt., sol. in ex., if no zinc is present. | A brownish black ppt. of sulphuret, formed slowly. |
| A brown ppt., sol. in ex. | A brownish yellow ppt. of sulphuret, sol. in ex., re-pptd. by HCl. | A brown ppt. of sulphuret, formed slowly. |
| The same as ammonia. | A yellowish brown ppt. of sulphuret, insol. in ex. | A yellowish brown ppt. of sulphuret, formed slowly. |
| The solution is decolorised, but no ppt. is produced. | A black ppt. of sulphuret, insol. in ex. | A black ppt. of sulphuret. |
| No precipitate. | A dark brown ppt. of sulphuret, sol. in large ex. | A black ppt. of sulphuret, formed slowly, slightly sol. in ex. |

| | Potash. | Carbonate of Potash. | Ammonia. |
|--|--|--|--|
| 16. Platinic oxide (perchloride). (See also p. 96.) | If HCl. is present, a yellow ppt., sol. in pot. if hot; insol. in dilute acids (a double chloride of plat. and potassium). | If HCl. is present, a yellow ppt., insol. in ex. (a double chloride of plat. and potassium). | From perchloride of plat., a yellow ppt., sol. in ex. if hot; insol. in dilute acids (a double chloride of plat. and am.). |
| 17. Rhodic oxide. (See also p. 96.) | No ppt. in the cold, but on ebullition, a gelat. brownish yellow ppt. of oxide falls. | As potash. | A yellowish ppt. containing am., sol. in HCl., formed very slowly. |
| 18. Silver, oxide of. (See also p. 97.) | A brown ppt. of oxide, insol. in ex., sol. in am. | A white ppt. of carbonate, sol. in am. | A brownish ppt. of oxide, very sol. in ex. |
| 19. Telluric oxide. (See also p. 98.) | A white ppt. of oxide, sol. in ex. | A white ppt. of oxide, sol. in ex. | A white ppt. of oxide, sol. in ex. |
| 20. Tin, protoxide of. (See also p. 98.) | A white ppt. of oxide, sol. in ex.; the soln. deposits metallic tin on being heated. | A white ppt. of oxide, insol. in ex. | A white ppt. of oxide, insol. in ex. |
| 21. Tin, peroxide of. (See also p. 99.) | A white ppt. of oxide, sol. in ex. | A white ppt. of oxide, sol. in large ex. | A white ppt. of oxide, sparingly sol. in ex. |

| Carbonate of Ammonia. | Hydrosulphate of Ammonia. | Sulphuretted Hydrogen (in an acid liquid). |
|--|---|--|
| If HCl. is present a yellow ppt. insol. in ex. (a double chloride of plat. and potassium.) | A brownish black sulphuret, sol. in a large ex., and in alkalies. | A brown ppt. of sulphuret in acid or neutral solns., formed very slowly. |
| As ammonia. | A brown sulphuret, insol. in ex. | A brown sulphuret, formed very slowly. |
| A white ppt. of carbonate, sol. in ex. | Black sulphuret, insol. in ex., in dilute acids, and in alkalies. | A black sulphuret, the same as produced by hydro-sulph. am. |
| A white ppt. of oxide, sol. in ex. | A brown sulphuret, very sol. in ex. | A brown ppt. of sulphuret, very sol. in alkaline sulphurets. |
| A white ppt. of oxide, insol. in ex., sol. in potash. | A brown sulphuret, slowly sol. in ex. | A brown sulphuret, sol. in pot. and in alkaline sulphurets. |
| A white ppt. of oxide, insol. in ex. | A yellow ppt. of bisulphuret, sol. in ex. in alkalies, alkaline carbonates, and hot concentrated HCl. | A yellow ppt. of bisulphuret, in acid solns. |

Additional remarks on the characters of such of the Third Class of Oxides as possess basic, and not acid properties.—The distinguishing character of the third class of metallic oxides is, that their acid solutions afford precipitates of metallic sulphurets when exposed to sulphuretted hydrogen. This class includes both metallic bases and metallic acids; for convenience, the characters of the bases and acids may be considered separately.

Of the precipitates of sulphurets produced in the acid solutions of this class of metallic oxides, by sulphuretted hydrogen, some completely dissolve in solutions of alkaline sulphurets, while others remain undissolved.

This difference in character is the basis of a subdivision of the members of this class, which is of frequent application in qualitative analysis. The sulphurets corresponding to the following oxides are *soluble* in solutions of alkaline sulphurets:—

| | |
|--------------------|-------------------|
| Oxide of antimony. | Platinous oxide. |
| Oxide of gold. | Platinic oxide. |
| Iridic oxide. | Telluric oxide. |
| Molybdous oxide. | Protoxide of tin. |
| Molybdic oxide. | Peroxide of tin. |

The sulphurets corresponding to the following oxides are *insoluble* in solutions of alkaline sulphurets:—

| | |
|------------------------------------|-------------------|
| Oxide of bismuth. | Osmic oxide. |
| Oxide of cadmium. | Palladious oxide. |
| Oxide of copper.* | Rhodic oxide. |
| Oxide of lead. | Oxide of silver. |
| Suboxide and protoxide of mercury. | |

The presence of alkaline cyanides (in excess), several organic acids, and organic matters in general, greatly interferes with the action of several reagents on solutions of some metals of this class, by preventing the formation of precipitates. Organic matters may be removed by incineration, and alkaline cyanides, by boiling the solution with hydrochloric acid.

* The sulphuret of copper is slightly soluble in hydrosulphate of ammonia, but not in sulphuret of potassium.

1. **OXIDE OF ANTIMONY.**—The compounds of oxide of antimony are usually colourless, or nearly so. Litmus paper is reddened by neutral solutions of salts of antimony.

Oxide of antimony is readily dissolved by hydrochloric acid with formation of chloride of antimony; but when this solution is diluted with much water, the chloride of antimony undergoes a remarkable decomposition, being resolved into an insoluble basic chloride, or compound of oxide and chloride of antimony, which precipitates as a white powder, and an acid chloride which still remains in solution. The precipitated basic chloride of antimony is soluble in tartaric acid and many other bodies of organic origin; hence the addition of one of these to the solution of chloride of antimony prevents the formation of a precipitate on dilution with water.

Metallic antimony is precipitated from a solution of the chloride of antimony by *metallic zinc*, in the form of a black powder. If sufficient free hydrochloric or sulphuric acid is present to cause a brisk evolution of hydrogen gas, a portion of the reduced antimony combines with hydrogen to form the gas known as antimonietted hydrogen, the properties of which are in some respects similar to arsenietted hydrogen gas. The characters in which antimonietted hydrogen and arsenietted hydrogen resemble and differ from each other, are pointed out in the Chapter on the Detection of Poisons.

Antimony is distinguished from other metals by the orange-red colour of its sulphuret; by the solubility of its sulphuret in solutions of alkaline sulphurets, and also in boiling hydrochloric acid; by the decomposition of a solution of chloride of antimony by dilution with water; by the solubility of the precipitated basic chloride in a hot solution of bitartrate of potash (cream of tartar); and by the appearances which oxide of antimony exhibits before the blowpipe. (See the Chap. on Blowpipe Analysis.)

2. **OXIDE OF BISMUTH.**—When a solution of a salt of bismuth, containing but little free acid, is mixed with water, the salt of bismuth is resolved, like the chloride of antimony, into an insoluble sub-salt, which is precipitated as a dense white powder, and a salt combined with excess of acid which

remains in solution. The precipitated sub-salts of bismuth are insoluble in tartaric acid, by which circumstance they are distinguished from the similar precipitates produced by the dilution of solutions of antimony. The presence of organic matters does not prevent the precipitation of salts of bismuth by dilution with water, nor by alkalies.

Metallic bismuth is precipitated from its solutions by a piece of *metallic zinc*, in the form of a black spongy mass. If sufficient free acid is present to cause a lively effervescence of hydrogen gas, a little of the bismuth combines with the hydrogen to form a gas analogous to antimonietted and arsenietted hydrogen. The manner of distinguishing this gas from arsenietted hydrogen is pointed out in the Chapter on the Detection of Poisons.

Iodide of potassium produces in solutions of bismuth an orange precipitate of iodide of bismuth, very soluble in an excess of iodide of potassium.

Chromate of potash produces in bismuth solutions a yellow precipitate of chromate of bismuth, which differs from the analogous precipitate of chromate of lead by being insoluble in a solution of caustic potash, and soluble in dilute nitric acid.

The principal characters by which bismuth may be distinguished from other metals are, the precipitability of its salts from their solutions by water, and the insolubility of the precipitated sub-salt in tartaric acid; the comportment of its solutions with hydrosulphate of ammonia; and the insolubility of its hydrated oxide in caustic potash.

3. OXIDE OF CADMIUM. — The soluble salts of cadmium are colourless; their neutral solutions redden litmus paper.

When *metallic zinc* is placed in a solution of cadmium, metallic cadmium is precipitated in bright grey spangles.

Non-volatile organic matters prevent the precipitation of oxide of cadmium by potash, but not of carbonate of the oxide of cadmium by alkaline carbonates.

The formation of a yellow sulphuret with sulphuretted hydrogen, and the insolubility of this sulphuret in solutions of alkaline sulphurets, is a characteristic property of salts of cadmium. (See the Chapter on Blowpipe Analysis.)

4. SUBOXIDE OF COPPER.—Hydrochloric acid is almost the only acid which dissolves suboxide of copper without decomposition. Sulphuric, and nearly all other acids, resolve suboxide of copper into metallic copper and protoxide of copper. Nearly all the compounds of suboxide of copper are either white, yellow, red, or brown; when exposed in solution to the air, they absorb oxygen, and become salts of protoxide of copper, possessing either a blue or green colour.

When a solution of subchloride of copper in hydrochloric acid is considerably diluted with water, the subchloride is precipitated as a white powder. It is re-dissolved by a fresh addition of hydrochloric acid.

A solution of *yellow prussiate* of potash produces in the hydrochloric acid solution of subchloride of copper a white precipitate, which becomes reddish-brown on exposure to the air. In a similar solution, *iodide of potassium* forms a white precipitate of subiodide of copper, and the supernatant liquor contains no free iodine, as happens when a salt of the protoxide of copper is substituted for one of the suboxide.

On the first addition of caustic potash to the hydrochloric acid solution of subchloride of copper, the subchloride is precipitated as a white powder; an excess of potash produces the appearance mentioned in the Table.

Suboxide of copper is distinguished from all other bodies by its comportment with ammonia. When this alkali is added in excess to a solution of the suboxide of copper, a colourless liquid is obtained, which contains the suboxide in solution; but on exposure to the air, the suboxide rapidly absorbs oxygen, and passes into the state of protoxide, and the liquid at the same time acquires a deep blue colour.

5. PROTOXIDE OF COPPER.—The hydrated salts of protoxide of copper are either green or blue; the anhydrous salts of the same oxide are either white or brown. The solutions of salts of protoxide of copper in water, or in acids, possess a blue or green colour, even when highly diluted. Litmus paper is reddened by neutral solutions of protoxide of copper.

Metallic iron, when placed in a solution of copper, precipi-

tates the latter metal with its characteristic colour. In a concentrated solution containing a little free acid, the copper is precipitated immediately in a pulverulent form; but from a dilute solution, the copper is precipitated more slowly, and as a coherent film on the piece of iron. The most convenient way of applying this test is to place the liquid under examination in contact both with iron and platinum, these two metals being also in contact, when copper, if present, is deposited as a red film on the platinum. In applying this test, a drop or two of the liquid may be placed on a clean piece of platinum foil, and both the liquid and the platinum touched with a bright piece of iron.

Iodide of potassium produces in a solution of a salt of protoxide of copper, a white precipitate of subiodide of copper, while the supernatant liquid contains free iodine. The subiodide of copper is soluble in an excess of iodide of potassium.

Yellow prussiate of potash produces in solutions of protoxide of copper a reddish-brown precipitate of ferrocyanide of copper, insoluble in hydrochloric acid. This test is not only very characteristic, but extremely delicate, as it forms a precipitate in very dilute solutions of copper.

Protoxide of copper may be distinguished from all other metallic oxides with great facility, by its comportment with ammonia (see the preceding Table), with yellow prussiate of potash, with hydrosulphate of ammonia, and with metallic iron. The blowpipe also affords ready means of detecting this metal. (See the Chap. on Blowpipe Analysis.)

The presence of many organic matters materially affects the indications of cupreous solutions with reagents, particularly with alkalis, the oxide of copper being preserved in solution by the organic matters, whatever excess of alkali is applied. Hydrosulphate of ammonia, however, when added to such an alkaline solution, produces a brown precipitate of sulphuret of copper, which should be collected on a filter, and examined before the blowpipe, or be dissolved in hot nitric acid, and the solution treated with the ordinary tests for copper. The indications of metallic iron and yellow prussiate of potash with salts of copper are not influenced by organic matters;

hence these are generally the most convenient tests to apply in such a case. The solution tested with either of these reagents should contain a little free acid. (See also the methods of detecting copper in organic mixtures, described in the Chapter on the Detection of Poisons.)

6. OXIDE OF GOLD. — The characters of the solution of gold noted in the preceding Table, are those of perchloride of gold. The combinations of oxide of gold with oxygen acids are almost unknown.

When the perchloride of gold is heated to a temperature of 400° or 500° F., it disengages a part of its chlorine, and becomes reduced to the state of protochloride of gold; at a higher temperature the whole of the chlorine is evolved, and metallic gold remains.

Litmus paper is reddened by a neutral solution of perchloride of gold.

Protosulphate of iron (copperas) is an appropriate reagent for the detection of gold in a neutral liquid. When mixed with a very dilute solution of gold, it produces at first a purple tint, or by reflected light, a green tint, which gradually disappears, when a dark brown precipitate of metallic gold makes its appearance. In a stronger solution, the precipitate of metallic gold is produced immediately.

Another very delicate test for gold in a liquid, is a solution of protochloride of tin containing a little perchloride of tin, rendered clear by the addition of a little hydrochloric acid. In an extremely weak solution of gold, this reagent produces, at first, a purplish red tint, and afterwards a violet precipitate, consisting of a compound of protoxide of gold and peroxide of tin (purple of Cassius). In a stronger solution, this precipitate is produced immediately.

Sulphurous acid is another extremely delicate test for gold, but it is not applicable to solutions containing free hydrochloric acid or much ammoniacal salts; the free acid, if any is present, should therefore be neutralized by potash or soda before this reagent is applied. In a highly diluted solution of gold it produces a blue colour, and when the liquid is boiled, a precipitate of metallic gold.

Oxalic acid also precipitates metallic gold from solutions of this metal, slowly in the cold, but more quickly if the mixture is heated.

Organic matters, in general, when introduced into a solution of gold, occasion the formation of a precipitate either of metallic gold or of protoxide of gold. By some of these bodies the reduction is effected almost instantaneously, but by others only after the lapse of some time.

7. IRIDIC OXIDE.—The characters of this oxide, as noted in the preceding Table, are those exhibited by a solution of perchloride of iridium. The solutions of this and all corresponding compounds of iridium possess a deep brownish-red colour, even when considerably diluted. Concentrated solutions are so dark as to appear opaque. The hydrated compounds of *protoxide of iridium*, and their solutions, generally possess a greenish colour.

A solution of *protosulphate of iron* decolorises a solution of perchloride of iridium, without the production of any immediate precipitate. After some time, a greenish precipitate is formed.

Oxalic acid produces no change in a solution of perchloride of iridium at first, but after standing for some time, the mixture loses its colour.

Protochloride of tin produces a brown precipitate in a solution of perchloride of iridium.

The principal characters by which metallic iridium is distinguished from other metals are, its insolubility in aqua regia, and in fused bisulphate of potash*; the deep brownish-red colour of the solution of its perchloride, and the peculiar comportment of that solution with caustic potash; and the easy reducibility of its compounds to the metallic state, by being heated in an atmosphere of hydrogen gas.

8. OXIDE OF LEAD.—The solutions of salts of lead are colourless, and redden litmus paper, though neutral in constitution.

* By fusion with bisulphate of potash, iridium is converted into suboxide; but this substance does not dissolve in the bisulphate. This test may be applied for the purpose of distinguishing iridium from rhodium (see page 96.), as the latter metal does dissolve in melted bisulphate of potash.

Sulphuric acid and a *solution of sulphate of soda* produce in solutions of lead a heavy white precipitate of sulphate of lead, insoluble in pure water and in diluted sulphuric acid, but slightly soluble in strong and dilute nitric acid, in many saline solutions, especially of ammoniacal salts, and in solutions of the acetates of potash and soda, and freely soluble in solution of caustic potash.

A solution of *chromate of potash* produces in solutions of lead a dense yellow precipitate of chromate of lead, insoluble in dilute nitric acid, but freely soluble in caustic potash. By contact with ammonia, the yellow chromate of lead acquires an orange colour, owing to the removal by the ammonia of a part of its chromic acid, and the formation of the subchromate of lead (chrome orange).

Iodide of potassium produces in solutions of lead a bright yellow precipitate of iodide of lead, soluble in a large excess of iodide of potassium and in hot water. If the lead solution is in excess, the precipitate is yellowish-white.

Hydrochloric acid and *solutions of chlorides* produce in tolerably strong solutions of lead a white precipitate of chloride of lead, which is soluble in a large quantity of water and in caustic potash. It is insoluble in, and is not blackened by ammonia.

Lead is very well characterised by the comportment of its solutions with sulphuretted hydrogen (see the preceding Table) and the reagents just mentioned.

The precipitate of sulphate of lead produced by sulphuric acid, is distinguished from the precipitate of sulphate of barytes, which is produced in like circumstances from solutions of barytes salts, by being blackened by hydrosulphate of ammonia, which sulphate of barytes is not. The precipitate of chloride of lead, produced by hydrochloric acid is distinguished from the white precipitates of chlorides formed by hydrochloric acid in solutions of silver and suboxide of mercury, by its comportment with ammonia. (See page 97.)

9. SUBOXIDE OF MERCURY.—The soluble salts of suboxide of mercury are colourless, and their neutral solutions redden litmus paper. Suboxide of mercury, the colour of which

is black, is converted by a moderate heat, into a mixture of metallic mercury and protoxide of mercury; by a dull red heat, the latter is resolved into oxygen gas and metallic mercury. Some of the neutral salts of suboxide of mercury, when mixed with water, are resolved into an acid salt, which dissolves, and an insoluble basic salt.

Hydrochloric acid and *solutions of chlorides* produce in solutions of the suboxide of mercury a white precipitate of subchloride of mercury (calomel), nearly insoluble in cold nitric and hydrochloric acids, but soluble in these acids by the aid of prolonged ebullition. When mixed with caustic potash or ammonia, this precipitate is converted to the black suboxide of mercury.

A solution of *chromate of potash* produces in solutions of suboxide of mercury a red precipitate of the chromate of the suboxide of mercury.

The presence of mercury in a liquid, whether in the state of suboxide or protoxide, is easily ascertained by placing a drop of the liquid, either neutral or slightly acid, on a bright plate of *copper*, when metallic mercury, if present, is deposited on the copper as a white coating, which acquires a metallic lustre by friction with paper. It disappears entirely when the copper is heated to dull redness, the mercury being thereby volatilised. If a drop of a solution containing mercury is placed on a piece of gilt paper, and both the drop and the gold are touched with a clean piece of iron, metallic mercury is deposited on the gold.

Protochloride of tin produces in solutions of both the suboxide and protoxide of mercury a grey precipitate of metallic mercury, which coheres into globules when heated with a little hydrochloric acid.

The comportment of suboxide of mercury, in solution, with hydrochloric acid, and of the precipitate produced thereby with ammonia, serve to distinguish this from all other metallic oxides.

10. PROTOXIDE OF MERCURY.—The soluble salts of protoxide of mercury are colourless, and their neutral solutions redden litmus paper. Some of the salts of this oxide, when mixed with water, are resolved into soluble acid salts,

and insoluble basic salts ; such is the case with the sulphate and nitrate.

When *potash* is added to a solution of protoxide of mercury, in quantity insufficient for the complete decomposition of the mercurial compound, a reddish-brown precipitate falls, consisting of a compound of oxide of mercury with the undecomposed mercurial salt. On applying an excess of potash, the precipitate becomes yellow, and then consists of hydrated protoxide of mercury. If the mercurial solution contains a large quantity of a free acid, potash produces either a slight whitish precipitate, or no precipitate at all. The presence of ammoniacal salts also materially affects the indications of potash with a solution of protoxide of mercury, the precipitate produced in such a case being white and composed of a subsalt of mercury in union with an ammoniacal compound ; the same body, in fact, as caustic ammonia itself precipitates.

The reddish-brown precipitate which *carbonate of potash* produces in solutions of peroxide of mercury, is a basic salt of this oxide which does not alter in colour or composition by an excess of the alkaline carbonate. In the presence of muriate of ammonia, carbonate of potash produces the same white precipitate as ammonia produces.

The comportment of a solution of the protoxide or protochloride of mercury with *sulphuretted hydrogen* and *hydrosulphate of ammonia* is very characteristic. When applied in very small quantity, these reagents throw down a greyish precipitate which becomes quite white on agitation, unless, too much of the reagent has been applied. On introducing a further quantity of sulphuretted hydrogen or hydrosulphate of ammonia, the precipitate at length becomes quite black and dense. The white precipitate produced by the first addition of the reagent, is a compound of sulphuret of mercury with some of the still undecomposed mercurial salt contained in the solution ; as a further quantity of the precipitate is introduced, the mercurial salt becomes entirely converted into a black sulphuret. The latter compound is insoluble in boiling hydrochloric and nitric acids, and in hydrosulphate of ammonia. It dissolves completely in caustic potash.

Iodide of potassium produces in a solution of protoxide of

mercury a yellow precipitate of iodide of mercury, which immediately on its precipitation assumes a brilliant scarlet colour. It is soluble in an excess of iodide of potassium, as well as in an excess of the mercurial salt, and also in hydrochloric acid.

Protochloride of tin, when applied in small quantity to a solution of protoxide of mercury, reduces the latter to a state of suboxide, and thus forms a precipitate of subchloride of mercury (calomel); an excess of protochloride of tin reduces the precipitated subchloride to metallic mercury. (See page 92.)

Metallic copper precipitates mercury from solutions of its protoxide as well as from solutions of the suboxide. (See page 92.)

Mercury is easily distinguished from all other metals by the comportment of the solution of its protoxide with sulphuretted hydrogen and iodide of potassium; and in the dry way it is readily detected in any of its compounds by the liberation of metallic mercury, when the mercurial compound is mixed with dry carbonate of soda, and the mixture heated before the blowpipe in a glass tube sealed at one end. The metal condenses on the sides of the tube as a grey crust which runs into globules on being touched with a glass rod.

The presence of organic matters considerably affects the indications of mercurial solutions with some reagents. (See a mode of detecting mercury in such a case, in the Chapter on the Detection of Poisons.)

11. MOLYBDIOUS OXIDE.—The characters belonging to this oxide, as noted in the preceding Table, are those of its solution in hydrochloric acid. This solution possesses a deep brown colour, even when largely diluted with water. The compounds of molybdenum are best recognised by their blowpipe characters. (See the Chapter on Blowpipe Analysis.)

12. MOLYBDIC OXIDE.—Both molybdic oxide and molybdous oxide are best recognised by their blowpipe characters. They may be distinguished from each other by the solubility of molybdic oxide in an excess of a solution of carbonate of potash being much greater than that of molybdous oxide.

13. OSMIC OXIDE.—The compounds of osmium are easily

recognised by the property which their solutions possess of disengaging, when boiled with nitric acid, the disagreeable odour of suboxide of osmium; and by their susceptibility of reduction by hydrogen gas to metallic osmium, which, as well as the oxide of this metal, exhales the characteristic odour of the suboxide whenever it is heated strongly in the air. (Rose.) When, however, the combinations of osmium are associated with iridium, they resist the action of nitric acid and of oxygen.

14. **PALLADIOUS OXIDE.**—The characters of a solution of palladious oxide, as noted in the preceding Table, are those of the chloride corresponding to this oxide, which is formed when metallic palladium is dissolved in aqua regia. The solution of this compound possesses a reddish-brown colour.

A solution of palladium is very well characterised by affording a yellowish white precipitate with a solution of *cyanide of mercury*, consisting of cyanide of palladium. In solutions containing free hydrochloric acid, this precipitate is formed either very slowly or not at all. By this reagent, in conjunction with those mentioned in the preceding Table, palladium may easily be distinguished from platinum and other metals. The presence of organic matters does not affect the action of cyanide of mercury on a solution of palladium, but it does that of alkalis.

15. **PLATINOUS OXIDE.**—The protochloride of platinum, which corresponds in constitution to platinous oxide, is a dark brown powder, insoluble in water, but soluble in a solution of perchloride of platinum, and in hydrochloric acid. The comportment of platinous oxide compounds with the reagents mentioned in the preceding Table, is that exhibited by the solution of the protochloride in hydrochloric acid. Platinum is detected more easily when in the state of perchloride, or a soluble compound of the peroxide (platinic oxide), than in that of the protochloride or platinous oxide; hence if the object is merely to discover the existence of platinum, it is proper to apply means for the conversion of the protochloride or platinous oxide compounds into the perchloride or platinic oxide, such as heating with a little aqua regia. The two oxides are easily distinguished from each other by the comportment of their solutions with ammonia.

16. PLATINIC OXIDE. — The neutral solutions of salts of platinic oxide redden blue litmus paper, but the double salts of the corresponding perchloride of platinum with alkaline chlorides do not. The perchloride of platinum is reduced to the state of protochloride when heated to about 600°, and to metallic platinum if heated still higher, free chlorine being expelled in each case.

Platinum in a state of solution, as platinic oxide, or the corresponding perchloride, is easily distinguished from every other metal by means of *chloride of potassium*, or *muriate of ammonia*, which reagents throw down a yellow, crystalline precipitate of double chloride of platinum and potassium, or chloride of platinum and ammonium, soluble in alkalis, but sparingly soluble in dilute acids. The same precipitates are produced when a little caustic potash or caustic ammonia is added to a solution of perchloride of platinum; but sufficient hydrochloric acid should be present to convert the alkalis into chlorides, otherwise the free alkali may prevent the precipitation of the double chloride.

A solution of *cyanide of mercury* produces no precipitate in a solution of perchloride of platinum.

17. RHODIC OXIDE. — Most of the soluble compounds of rhodium possess a peculiar rose-colour. The solutions of rhodic oxide in hydrochloric and concentrated sulphuric acid have a yellow colour; but the residues obtained on evaporation to dryness are red, and communicate a rose tint to water when dissolved in that liquid.

When compounds containing rhodium are heated in an atmosphere of hydrogen gas, they become reduced to metallic rhodium, which is recognised by its insolubility in aqua regia, and by its solubility in melted bisulphate of potash. In applying this test the mixture of the reduced metal and bisulphate of potash may be heated nearly to redness in a hard glass tube sealed at one end. The colour of the mass, when solid, is yellow, if rhodium is present. Silver and palladium are the only noble metals * which dissolve in melted bisulphate of potash (Rose). Rhodium is also distinguished

* Noble metals* are those which do not become converted into oxides, but remain bright when heated in the air.

from most other metals by the comportment of its solution with potash and ammonia.

18. OXIDE OF SILVER.—The soluble neutral salts of oxide of silver are colourless, do not affect the colour of litmus paper, and are decomposed at a red heat. Several silver compounds, both soluble and insoluble, blacken on exposure to light.

The precipitation of oxide of silver by several reagents is prevented by the presence of ammoniacal salts, soluble cyanides, hyposulphites, and some other salts.

Hydrochloric acid, and *solutions of chlorides*, produce, in solutions of silver, a white, curdy, precipitate of chloride of silver, insoluble in dilute acids, but very soluble in ammonia, from which solvent it is re-precipitated on saturating the alkali by an acid. In an extremely dilute solution of silver, hydrochloric acid produces an opalescence; but after a time the precipitate subsides, and the liquid becomes clear. Chloride of silver blackens on exposure to light, and fuses at a temperature below redness. The solidified chloride is transparent, and has some resemblance to horn.

Iodide of potassium produces, in solutions of silver, a yellowish-white precipitate of iodide of silver, soluble in an excess of iodide of potassium, but scarcely at all soluble in ammonia, and in dilute nitric acid.

Protosulphate of iron occasions in neutral solutions of silver a white precipitate of metallic silver. *Chromate of potash* produces a reddish-brown precipitate of chromate of silver, soluble in ammonia, and in dilute nitric acid.

Silver compounds, when heated with carbonate of soda before the blowpipe, are readily reduced to metallic silver, which is recognised by its whiteness and ductility.

The only metals besides silver whose solutions afford precipitates of chlorides by hydrochloric acid, are mercury, when in the state of suboxide, and lead. Of the precipitated chlorides, that of silver alone is soluble in ammonia. If chloride of lead, subchloride of mercury, and chloride of silver are precipitated together, the whole of the chloride of silver may be dissolved out of the precipitate by digesting the latter in ammonia, and it may be re-precipitated by neutralizing the ammoniacal solution with hydrochloric acid.

19. **TELLURIC OXIDE.**—The salts of telluric oxide are, for the most part, decomposed and volatilised when heated to redness. Telluric oxide, which is white when cold, but yellow when hot, melts at a temperature below redness, and volatilises completely at a higher temperature as a white smoke, without forming any crystalline sublimate. The strong solution of telluric oxide in hydrochloric acid deposits a basic salt on dilution with water, like chloride of antimony. The precipitated basic salt re-dissolves on the introduction of more hydrochloric acid. The solution of telluric oxide in nitric acid, does not become decomposed in this manner by dilution with water (Rose).

A solution of *sulphurous acid* or of an *alkaline sulphite*, and a bar of *metallic zinc*, produce a black precipitate of metallic tellurium in solutions of telluric oxide.

The compounds of tellurium are easily recognised by their blowpipe characters (see the chapter on Blowpipe Analysis); and also by the comportment of the solution of telluric oxide with sulphuretted hydrogen, hydrosulphate of ammonia, and alkaline carbonates. No other oxide behaves as telluric oxide with all these reagents. (See the preceding Table.)

20. **PROTOXIDE OF TIN.**—The soluble proto-salts of tin redden litmus paper, though neutral in constitution; are colourless, and are decomposed by being heated to redness. The protochloride and some other proto-salts of tin, undergo a partial decomposition when mixed with water, into soluble acid salts, and insoluble basic salts. The latter are dissolved on the application of hydrochloric acid.

An extremely delicate test for proto-salts of tin is *perchloride of gold*, which produces a purple precipitate of a compound of peroxide of tin and protoxide of gold, known as purple of Cassius. As the mixture should contain a little peroxide of tin, it is advisable to add with the perchloride of gold a small quantity of nitric acid, to peroxide a portion of the protoxide of tin, but the application of heat should be avoided. (See page 98).

A solution of *protochloride of mercury* produces in solutions of proto-salts of tin a white precipitate of subchloride of

mercury: the proto-salt of tin here becomes a per-salt, through acquiring half of the chlorine of the protochloride of mercury.

Proto-salts of tin are readily distinguished from all the bodies with which they are likely to be confounded, by their comportment with perchloride of gold.

21. PEROXIDE OF TIN.—The precipitate of hydrated peroxide of tin, produced by alkalis in solutions of salts of the peroxide of tin is readily soluble in acids and in caustic potash; but the hydrated peroxide of tin formed by the action of nitric acid on metallic tin is quite insoluble in these liquids, as is likewise the precipitated oxide after being heated to redness. It is hence inferred that peroxide of tin exists in two different states, distinguished from each other by their relation to solvents. The insoluble peroxide may be converted into the soluble by fusion with alkalis or alkaline carbonates. The neutral soluble salts of peroxide of tin redden litmus paper, and are colourless.

In a solution of a per-salt of tin, containing some free nitric acid, a bar of *metallic zinc* produces a white gelatinous precipitate of hydrated peroxide of tin, with disengagement of hydrogen gas. If no free nitric acid is present, zinc produces a precipitate of metallic tin.

Free acids occasion, in the solution of bisulphuret of tin in hydrosulphate of ammonia (see the preceding Table), a yellow precipitate consisting of the unaltered bisulphuret. When the solution of the same sulphuret in caustic potash is boiled with oxide of copper, sulphuret of copper and peroxide of tin are formed; the peroxide remains in solution.

Tin in solution as peroxide may be distinguished from nearly all other metals by its comportment with sulphuretted hydrogen and hydrosulphate of ammonia. By these reagents, however, it may be confounded with arsenic and antimony, but the blowpipe affords a ready and safe means of determining the presence or absence of tin in compounds containing both arsenic and antimony. (See the chapter on Blowpipe Analysis.)

Compounds of peroxide of tin, which are insoluble in hydrochloric acid, may be rendered soluble in that acid by first fusing them in a platinum crucible with two or three times their weight of dry carbonate of soda..

SECTION II. METALLIC OXIDES OF THE

| Acids (in combination). | Nitrate of Silver (in alkaline salts of the acids). | Chloride of Barium (in alkaline salts of the acids). | Nitrate of Lime (in alkaline salts of the acids). |
|---------------------------------------|--|---|--|
| 1. Antimonie. (See also p. 102.) | A white ppt. | A white ppt. | A white ppt. |
| 2. Antimonious. (See also p. 104.) | Ditto. | A white ppt., slightly sol. in water. | A white ppt., slightly sol. in water. |
| 3. Arsenic. (See also p. 104.) | A chocolate red ppt., sol. in nitric acid, sol. in am. (arseniate of silver). | A white ppt., sol. in acids, sol. in mur. am. (arseniate of barytes). | A white ppt., sol. in HCl., in mur. am., and in hot water (arseniate of lime). |
| 4. Arsenious. (See also p. 106.) | A pale yellow ppt. of arsenite of silver, sol. in acetic acid, sol. in am.: the <i>ammonio-nitrate of silver</i> gives the same ppt. with free arsenious acid. | A white ppt. of arsenite of barytes formed very slowly in dilute solns. Free arsenious acid gives no ppt. | A white ppt. of arsenite of lime. Free arsenious acid gives no ppt. |
| 5. Molybdic. (See also p. 109.) | A white ppt., sol. in much water, nitric acid and am. | A white ppt., sol. in much water; sol. in NO_5 . | A white ppt., sol. in water, in HCl., and in NO_5 . |
| 6. Osmic. (See also p. 110.) | A brown ppt. | A brown ppt. | A brown ppt. |

THIRD CLASS, POSSESSING ACID PROPERTIES.

| Sulphuretted Hydrogen (in acid soln.). | Hydrosulphate of Ammonia. | Hydrochloric Acid. |
|--|--|---|
| An orange yellow sulphuret, sol. in alkalis, insol. in cold HCl. | An orange yellow sulphuret, sol. in ex. | A white ppt. of antimonious acid from antimoniate of pot. |
| Ditto. | Ditto. | A white ppt. of antimonious acid. |
| A yellow sulphuret, sol. in alkalis and alkaline sulphurets. | A yellow sulphuret on adding an acid to the mixture. | No change. |
| Ditto: the precipitated sulphuret is slightly sol. in pure water. | Ditto. | No change. |
| A brown ppt. of sulphuret, slow to subside, sol. in alkaline sulphurets. | A brown ppt. of sulphuret on adding an acid. | A white ppt. of molybdic acid in a strong solution, sol. in much water. |
| A brownish black sulphuret, insol. in alkaline sulphurets. | A black sulphuret, insol. in ex. | Free osmic acid, detected by its odour. |

| Acids (in combination). | Nitrate of Silver (in alkaline salts of the acids). | Chloride of Barium (in alkaline salts of the acids). | Nitrate of Lime (in alkaline salts of the acids). |
|--|--|--|---|
| 7. Selenious. (See also p. 111). | A white ppt., slightly sol. in NO_5 . | A white ppt., sol. in HCl . | A white ppt., sol. in NO_5 . |
| 8. Tungstic. (See also p. 111.) | A white ppt. | A white ppt. | A white ppt. |
| 9. Vanadic. (See also p. 112.) | A bulky yellow ppt., sol. in NO_5 , and in am. It bleaches on exposure. | A bulky orange yellow ppt., slightly sol. in water. | No ppt. |

Additional observations on the characters of metallic oxides of the third Class (that is, such as are precipitated by sulphuretted hydrogen from their acid solutions), possessing acid properties.—Of the oxides belonging to this class, some are soluble and others insoluble in water; but all are soluble in free alkalies, though some do not dissolve unless an excess of alkali is present. The precipitates produced in their acid solutions by sulphuretted hydrogen are generally sulphurets, corresponding in constitution to the metallic acid previously in solution, that is, containing as many equivalents of sulphur as the metallic acid contains of oxygen.

The comportment of these acids with solutions of nitrate of silver, chloride of barium, and nitrate of lime, as noted in the above Table, are such as are perceived with alkaline salts of the respective acids as nearly neutral as they can be prepared.

1. **ANTIMONIC ACID.**—Hydrated antimonie acid is insoluble in water and in nitric acid; it dissolves in strong hydrochloric acid, with the aid of heat, forming a solution which becomes milky when largely diluted with water, owing to the precipi-

| Sulphuretted Hydrogen (in acid soln.). | Hydrosulphate of Ammonia. | Hydrochloric Acid. |
|---|---|---|
| A yellow ppt., sol. in hydrosulph. am. (sulphuret of selenium). | A yellow ppt., sol. in ex. | No change. |
| A slight turbidity. | A brown ppt., dilute HCl. being present. | A white ppt., insol. in ex. (tungstic acid). |
| A greyish ppt. of vanadic oxide, in an aqueous soln. of vanadic acid. | The soln. becomes brown; HCl. produces in the mixture a brown ppt. of persulphuret of vanadium. | Chlorine is evolved: the mixture is capable of dissolving gold. |

tation of hydrated antimonic acid. When antimonic acid is strongly heated, alone, it disengages oxygen gas, and is reduced to the state of antimonious acid.

Antimonic acid forms with potash a sparingly soluble salt having an excess of acid, and a soluble neutral salt.

These combinations are formed by digesting hydrated antimonic acid in a solution of caustic potash, or by fusing antimonic acid with potash or carbonate of potash.

Antimoniate of soda possesses a very slight degree of solubility in water, on which account antimoniate of potash is employed as a precipitant for soda. (See page 32.)

When solutions of *potash*, *ammonia*, *carbonate of potash*, and *bicarbonate of potash* are mixed with the solution of antimonic acid in hydrochloric acid, white precipitates are produced, which re-dissolve, though not always completely, in an excess of the precipitant. The precipitate is re-dissolved most completely by potash. From this solution hydrochloric and almost all other acids precipitate the hydrate of antimonic acid, or an antimoniate of potash with excess of acid.

After antimonious acid and the greater number of antimonates have been heated to redness they are no longer soluble in acids; but their solubility is restored by fusing them with potash or carbonate of potash.

Antimonious acid is distinguished from nearly all other bodies by its comportment with hydrosulphate of ammonia and sulphuretted hydrogen. (p. 99.) The pure acid is recognized by the appearances it assumes when strongly heated in a glass tube sealed at one end: as soon as the whole of the water is disengaged from the *white* hydrate, *yellow* antimonious acid remains, which, when heated more strongly, becomes reduced to *white* antimonious acid with disengagement of oxygen gas, which is recognized by introducing into the tube the glowing extremity of a match just ignited and blown out.

2. ANTIMONIOUS ACID.—Antimonious acid and its hydrate are insoluble in water and in nitric acid, but are slowly dissolved by hot concentrated hydrochloric acid. From its solution in hydrochloric acid antimonious acid is precipitated by water as a hydrate. The colour of antimonious acid, both in the hydrated state and dry, is white. It may be heated either in the open air or in close vessels without suffering any change except the acquisition of a feeble yellow colour, which disappears on cooling. With the *fixed alkalis*, *alkaline carbonates*, *sulphuretted hydrogen*, and *hydrosulphate of ammonia*, antimonious acid behaves in just the same manner as antimonious acid.

Both antimonious and antimonious acids redden moistened litmus paper, whether in their hydrated state or after being calcined.

Antimonious acid in the free state is distinguished from oxide of antimony by its more difficult solubility in hydrochloric acid, and by neither fusing nor volatilizing when strongly heated. It is distinguished from antimonious acid by its white colour, and by not disengaging oxygen gas when heated to redness.

3. ARSENIC ACID. — The compounds of arsenic acid with bases are not volatile, even at a strong heat, unless they contain a volatile base; but several which contain an excess of acid disengage a portion of their arsenic acid at a high tem-

perature, the acid being resolved, on its expulsion, into oxygen gas and arsenious acid. Free arsenic acid is decomposed in the same manner at a high temperature. The compounds of arsenic acid, with nearly all bases except the alkalis, are insoluble in water.

A solution of *nitrate of silver* does not produce the same chocolate-red precipitate of arseniate of silver in a solution of arsenic acid as it does in a solution of neutral arseniate (as mentioned in the preceding Table), because the nitric acid liberated from nitrate of silver by arsenic acid retains the arseniate of silver in solution. But the *ammonio-nitrate* of silver (p. 36.) produces the same chocolate precipitate of arseniate of silver in a solution of free arsenic acid as nitrate of silver produces in a solution of an arseniate.

A solution of *nitrate or acetate of lead* produces in solutions of neutral arseniates a white precipitate of arseniate of lead, soluble in nitric acid.*

A neutral solution of *sulphate of copper* produces in neutral solutions of arseniates a blueish-green precipitate of arseniate of copper, which is also produced in a solution of free arsenic acid by the ammonio-sulphate of copper.

Sulphuretted hydrogen produces no precipitate in alkaline or neutral solutions of an arseniate; but if hydrochloric or other free acid is present a yellow precipitate of sulpharsenic acid falls, which is soluble in solutions of alkaline sulphurets, free alkalis, and carbonates of potash and soda. In dilute solutions, the whole of the sulpharsenic acid does not precipitate for several hours, but its subsidence is promoted by ebullition. Arsenic existing in a solution in the state of arsenic acid is not precipitated so completely by sulphuretted hydrogen as when it exists in the state of arsenious acid; on which account it is sometimes necessary to reduce arsenic acid to the

* The compounds of arsenic acid with bases generally bear considerable resemblance to the corresponding compounds of phosphoric acid; so that, unless the test of sulphuretted hydrogen is applied, arsenic and phosphoric acids may sometimes be compounded with each other. Arseniate of lead may be distinguished from phosphate of lead by its blowpipe characters. The former does not crystallize after fusion on charcoal before the blowpipe as the latter does, but is reduced, in the interior flame, to metallic lead, with disengagement of fumes of arsenic.

state of arsenious acid before applying sulphuretted hydrogen. This may easily be effected by heating the solution of arsenic acid with sulphurous acid, when the latter becomes sulphuric acid at the expense of a portion of the oxygen of the former.

The existence of arsenic in the precipitate produced by sulphuretted hydrogen may be confirmed by heating the precipitate with a mixture of carbonate or soda and cyanide of potassium, as described at p. 108.

In solutions of neutral arseniates, *hydrosulphate of ammonia* produces no precipitate, or nothing more than a faint troubling, which is instantly removed by a further addition of the hydrosulphate; but on adding hydrochloric acid to the mixture, a yellow precipitate of sulpharsenic acid appears.

Arsenic acid is distinguished from nearly all other bodies by its comportment with sulphuretted hydrogen and hydrosulphate of ammonia: from peroxide of tin, and a few other oxides with which it might be confounded by those reagents, it is readily distinguished by the blowpipe. (See the chapter on Blowpipe Analysis, and also that on the Detection of Poisons.)

A solution of *sulphate of copper* in the presence of an excess of *caustic potash* may be used as a means of distinguishing between arsenic acid and arsenious acid, the protoxide of copper being reduced to suboxide by arsenious acid, which passes into the state of arsenic acid. The liquid to be tested in this manner should be mixed with an excess of caustic potash, and then with a drop or two of a solution of sulphate of copper. The presence of a very minute quantity of arsenious acid causes the formation of a red precipitate of suboxide of copper.

For the means of discovering the presence of arsenic acid in an organic fluid, see the chapter on the Detection of Poisons.

4. ARSENIOS ACID. — Free arsenious acid possesses but a slight degree of solubility in cold water, but is much more

degree considerably below redness, as a colourless vapour, which deposits, on a cold body, minute octohedral crystals of arsenious acid. The vapour of arsenious acid is inodorous: the peculiar alliaceous odour sometimes perceived in arsenical fumes seems to be due to a lower oxide of arsenic. All the arsenites, or combinations of arsenious acid with bases, excepting the alkalis, are insoluble in water, or nearly so, but soluble in acids. When heated to redness, arsenites are generally resolved into arseniates, with disengagement of arsenic vapour.

The yellow precipitate of arsenite of silver produced in a neutral solution of arsenious acid by *nitrate of silver*, and by *ammonio-nitrate of silver* in free arsenious acid (see the preceding Table), is not produced in a solution of free arsenious acid by nitrate of silver.

Sulphate of copper produces a bright green precipitate of arsenite of copper in a neutral solution of arsenious acid, but none in the free acid; a solution of ammonio-sulphate of copper* affords the same precipitate in an aqueous solution of the free acid.

The test for arsenic which deserves most confidence is *sulphuretted hydrogen* (see the preceding Table), the precipitated sulpharsenious acid being always, in medico-legal investigations, collected and further examined by processes of reduction. The liquid to which this test is applied should be strongly acidified by hydrochloric acid, as sulpharsenious acid is slightly soluble in a neutral, or even feebly acid, liquid. Alkaline solutions of arsenious acid afford no precipitate whatever with sulphuretted hydrogen. Sulpharsenious acid dissolves not only in solutions of caustic alkalis and alkaline sulphurets, but in solutions of alkaline carbonates and bicarbonates. It is insoluble in hydrochloric acid and in cold dilute nitric acid, but is dissolved with decomposition by boiling nitric acid.

A solution of free arsenious acid in water affords no pre-

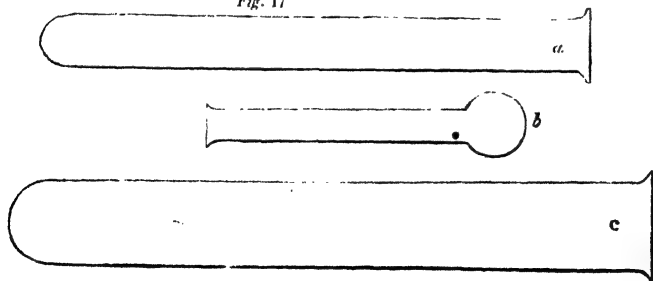
* This solution is prepared in the same manner as ammonio-nitrate of silver (see p. 36.), with sulphate of copper instead of nitrate of silver.

precipitate with *hydrosulphate of ammonia*, but on adding an acid to the mixture, sulpharsenious acid is precipitated.

To determine whether the precipitate produced by sulphuretted hydrogen is sulpharsenious acid or sulpharsenic acid, it may be dissolved in pure caustic potash, and the solution boiled with oxide of copper. The arsenical sulphuret is thereby decomposed with formation of sulphuret of copper, which is insoluble in the alkaline liquid, and either arsenious acid or arsenic acid, which remains in solution. After being filtered from the sulphuret of copper, the liquid is exactly neutralized with nitric acid, and tested with a solution of nitrate of silver: if a chocolate-red precipitate falls, the arsenical sulphuret was sulpharsenic acid; but if the precipitate with nitrate of silver is pale yellow, the arsenical sulphuret was sulpharsenious acid.

To obtain metallic arsenic from the precipitated sulphuret, the latter is intimately mixed either with twice its weight of dry black flux (a mixture of carbonate of potash and charcoal, prepared by heating cream of tartar to redness in a covered crucible), or, what is better, with about twelve times its weight of a mixture of three parts of dry carbonate of potash and one part of cyanide of potassium (Fresenius and Babo). The mixture, being perfectly dry, is placed in the sealed end of a tube of the form and size of *a* or *b*, exhibited below, and

Fig. 17



heated to redness by the flame of a spirit-lamp, on which metallic arsenic is disengaged in vapour, and condenses on the side of the tube as a bright mirror. As a further con-

mirror thus obtained may be taken out, placed in the bottom of the wide tube, *c*, and heated by a spirit-lamp, when the arsenic rises in vapour and becomes oxidized by the air in the tube, and crystals of arsenious acid condense on the cold part of the tube.

When black flux is employed for the reduction of sulphuret of arsenic in the above processes, only one-half of the arsenic is separated in the metallic state, the other half remaining in combination with soda; but when the mixture of cyanide of potassium and carbonate of potash is employed, the whole of the arsenic is liberated. ✓

In applying the above process to the detection of arsenic in cases of poisoning, certain precautions are to be observed, which will be noticed in the chapter on the Detection of Poisons. In the same chapter are also described easy methods for the detection of arsenic, by the production of arseni-*etted* hydrogen gas (Marsh's test), and by boiling an arsenical liquid with a plate of metallic copper (Reinsch's test.)

When arseniates, arsenites, and arsenious acid are mixed with carbonate of soda, and heated on charcoal in the interior blowpipe flame, a very characteristic alliaceous odour is exhaled, probably due to an oxide of arsenic inferior to arsenious acid. If the material to be operated on is very small in quantity, it should first be submitted to the process above described for the production of metallic arsenic, by heating with carbonate of potash and cyanide of potassium in a glass tube, as this test affords a more trustworthy result than any other.

5. MOLYBDIC ACID. — Molybdic acid is slightly soluble in water, and readily soluble in hydrochloric acid, nitric acid, solutions of caustic alkalies, and solutions of carbonated alkalies. Pure molybdic acid is a white mass, having a crystalline texture, which fuses when strongly heated in a close vessel, becoming a yellow liquid. When strongly heated in the open air it volatilizes, and may be condensed in crystals.

The first application of *sulphuretted hydrogen* to a solution of molybdic acid containing a free acid does not produce the brown precipitate mentioned in the preceding Table, but merely a blue or brown liquid; an *excess* ~~of the same~~ *etted*

hydrogen being necessary to the production of a precipitate. The sulphuret of molybdenum is very slow to subside in the cold; but if heat is applied it soon falls, and the liquid, previously greenish, becomes colourless. The sulphuret of molybdenum is converted by ignition in the open air into molybdic acid, which may be recognized by its blowpipe characters. (See the chapter on Blowpipe Analysis.)

A solution of *protochloride of tin* produces in a solution of an alkaline molybdate a blueish-green precipitate, soluble in hydrochloric acid.

When a bar of *metallic zinc* or *tin* is placed in a solution of molybdic acid containing hydrochloric acid, the liquid acquires a dark-brown colour owing to the reduction of molybdic acid to the state of molybdous oxide. If the brown liquid thus obtained is mixed with a larger quantity of a solution of an alkaline molybdate, the colour changes to blue, through the formation of the molybdate, of molybdic oxide, and if hydrochloric acid is not present in sufficient quantity, a blue precipitate is likewise produced. If the blue liquid is boiled with an excess of caustic potash, the blue colour disappears, a brownish-black precipitate of molybdic oxide falls, and molybdate of potash remains in solution (Rose).

6. OSMIC ACID.—Pure osmic acid forms at common temperatures a white crystalline mass, which fuses when gently warmed. At a somewhat higher temperature it volatilizes, and may be re-condensed in crystalline needles. It is but slightly soluble in water. The dry acid, as well as its aqueous solution, possesses a peculiarly pungent and disagreeable odour, highly irritating to the nose and eyes, by which character this acid may be distinguished from all other bodies. This odour is not possessed by compounds of osmic acid with bases, but it is immediately exhaled when such compounds are mixed with hydrochloric or nitric acid; and if such a mixture is distilled an aqueous solution of osmic acid may be obtained. Most compounds of osmic acid with bases (osminates) are either yellow or brown.

metallic osmium or a suboxide of osmium. The solution of osmic acid acquires, in these cases, a dark brown or violet colour, which disappears, however, on the subsidence of the precipitate. Protosulphate of iron, alcohol, acetic acid, and even ammonia, if in excess, are capable of effecting this reduction. In the case of protosulphate of iron a brown precipitate is formed immediately; with alcohol and acetic acid no immediate change takes place, but after some time a violet precipitate of metallic osmium makes its appearance.

7. **SELENIOUS ACID.**—Selenious acid is very soluble in water, and its hot concentrated aqueous solution deposits crystals similar to nitre on cooling. These crystals sublime at a temperature approaching 600° .

When a solution of selenious acid, or of a selenite, either in water or in hydrochloric acid, is mixed with an aqueous solution of *sulphurous acid*, the selenious acid is reduced with liberation of selenium as a red powder, which remains for some time in suspension in the liquid. If the mixture is boiled for a considerable time, the particles of selenium aggregate and become darker in colour. A solution of a selenite affords a precipitate of selenium when heated with a solution of muriate of ammonia.

Metallic zinc also causes a precipitate of selenium in a solution of selenious acid, or of a selenite containing a free acid.

Solid selenites, mixed with *muriate of ammonia* and heated in a small tube retort, afford a sublimate of selenium, which is recognized by the powerful odour of decayed cabbage possessed by its vapour. (See the behaviour of seleniates and selenites before the blowpipe).

8. **TUNGSTIC ACID.**—Tungstic acid is insoluble in water and in acids; with the fixed alkalies it forms compounds which are soluble in water. It does not volatilize when strongly heated, and possesses a yellowish tinge.

Sulphuric, hydrochloric, and nitric acids produce, in solutions of alkaline tungstates, white precipitates, consisting of compounds of tungstic acid with the acids applied as the precipitants, which are nearly insoluble in an excess of the acids. By the latter property, these precipitates are distinguished

from the similar precipitates produced in solutions of alkaline molybdates by the same acids.

When a bar of *metallic zinc* is placed in a solution of an alkaline tungstate, mixed with a slight excess of hydrochloric (or, what is better, phosphoric) acid, a fine blue colour is developed similar to that produced in the same way in a solution of titanio acid. In applying this test, it is not essential for the tungstic acid to be in a state of solution, as the recently precipitated acid soon affords the blue colour by contact with zinc. Tungstic acid is distinguished from titanio acid by the solubility in water of alkaline tungstates, alkaline titanates being nearly insoluble in water.

When compounds of tungstic acid with bases are digested in hydrochloric or nitric acid the bases generally dissolve, and leave the tungstic acid undissolved. Such tungstates as are not acted on by acids are best decomposed by fusing them, in a platinum crucible, with three times their weight of carbonate of potash or soda. When the resulting mass is digested in water an alkaline tungstate dissolves, while the base, previously in combination with tungstic acid, remains undissolved.

9. VANADIC ACID. -- Pure vanadic acid possesses a yellow or red colour according to its state of division; it fuses at a red heat, without volatilization or reduction (if contact with deoxidizing agents is avoided), and crystallizes on cooling. Vanadic acid is soluble in acids, but only slightly soluble in water. The compounds of vanadic acid with alkalies are not very soluble in water, particularly if much alkaline salts be present. Vanadate of ammonia is nearly insoluble in a solution of muriate of ammonia.

Vanadic acid, in solution, is reduced to the state of vanadic oxide by deoxidizing agents with great facility, the liquid thus acquiring a blue colour. Even hydrochloric acid, and, according to Rose, nitrous acid effect this reduction; the former with evolution of free chlorine, and the latter with formation of nitric acid. The free chlorine which is disengaged when hydrochloric acid is mixed with vanadic acid

Vanadic acid and vanadiates possess considerable resemblance to chromic acid and the corresponding chromates; both vanadic and chromic acids, for instance, are red, form yellow combinations with bases which become red when mixed with an acid, and afford blueish-green solutions by deoxidizing agents. These bodies may be distinguished by the following characters:—1. Solutions of vanadiates lose their colour by the application of heat, but solutions of chromates do not; 2. Dry vanadic acid, by exposure to a red heat, undergoes no change, but chromic acid disengages oxygen, and becomes reduced to the green oxide of chromium when heated to redness; 3. Chromic acid is very soluble in water, but pure * vanadic acid is nearly insoluble.

* Vanadic acid dissolves in water if vanadic oxide is also present, in which case the colour of the solution is green.

CHAPTER IV. *Behaviour of CHROMIC, HYPER-*

| Acids (in combination). | Nitrate of Silver (in alkaline salts of the acids.) | Chloride of Barium (in alkaline salts of the acids). | Nitrate of Lime (in alkaline salts of the acids). |
|---|--|--|--|
| 1. Chromic. (See also below.) | A reddish brown ppt. of chromate of silver, sol. in NO_3 and in am. | A canary yellow ppt. of chromate of barytes, sol. in NO_3 . | No ppt., except in concentrated solutions. |
| 2. Hypermanganic. (See also p. 116.) | A yellowish brown precipitate, sol. in much water. | No ppt. | No ppt. |
| 3. Manganic. (See also p. 117.) | A black ppt. of perox. of manganese. | No ppt. | A black ppt. of perox. of manganese. |

ADDITIONAL OBSERVATIONS ON THE CHARACTERS OF CHROMIC, HYPERMANGANIC, AND MANGANIC ACIDS.

These three acids are not included in the class whose characters form the subject of the preceding chapter, in consequence of their not being precipitated by sulphuretted hydrogen from acidified solutions.

1. CHROMIC ACID. — Pure chromic acid has a red colour, is very soluble in water, and is decomposed when heated to redness, with disengagement of oxygen gas, leaving a residue of green oxide of chromium. The compounds of chromic

MANGANIC, and MANGANIC Acids with Reagents.

| Sulphuretted Hydrogen. | Hydrosulphate of Ammonia. | Hydrochloric Acid. |
|---|---|--|
| Chromic acid is reduced to oxide of chromium, with precipitation of sulphur. | A greenish ppt. of oxide of chromium. | Chlorine is evolved, and chromic acid is reduced to oxide of chromium. |
| In neutral solns. a flesh-coloured ppt. of sulphur and persulphuret of manganese. | A flesh-coloured ppt. of persulphuret of manganese, insol. in ex. | Free chlorine is evolved and protochloride of manganese formed. |
| Ditto. | Ditto. | Ditto. |

a red or lively yellow colour. When sulphuric acid is added to a yellow solution of a chromate, a bichromate is formed, and the solution acquires a red colour.

Chromic acid is reduced to the state of green oxide of chromium, with great facility, by *deoxidizing agents*.

When chromic acid or a chromate is heated with *hydrochloric acid*, the mixture becomes green (owing to the formation of oxide of chromium), and disengages free chlorine; if alcohol is added, the reduction takes place more rapidly, with evolution of hydrochloric ether. Sulphurous acid, and the organic acids, also cause the reduction of chromic acid to oxide of chromium.

of a chromate containing a free acid, the chromic acid is reduced to oxide of chromium; if sufficient free acid is present to combine with the oxide of chromium thus formed, no precipitate is produced excepting sulphur, but if not, some of the oxide of chromium falls as a greenish precipitate.

Solutions of chromates afford, with a solution of *acetate of lead*, a bright yellow precipitate of chromate of lead (chrome-yellow), freely soluble in caustic potash, slightly so in nitric acid, and which changes to the red subchromate of lead (chrome-orange) by contact with ammonia.

Chromic acid and soluble chromates are well characterised by the colour of their solutions, and by the facility with which they afford a green solution of oxide of chromium by the action of deoxidizing agents. Insoluble chromates are detected by fusion with a mixture of carbonate of soda and nitre: when the resulting mass is digested in water, a yellow solution of an alkaline chromate is obtained, which becomes orange red by the addition of sulphuric acid, and green when heated with hydrochloric acid and alcohol.

2. HYPERMANGANIC ACID.—Hypermanganic acid and its combinations with bases are soluble in water, to which they communicate an intense and characteristic crimson colour. These bodies possess but little stability when in solution. Hypermanganic acid in solution is resolved, when heated, into oxygen gas and a precipitate of hydrated peroxide of manganese, the liquid losing its colour entirely: solutions of most permanganates are more stable than those of the free acid.

Organic matters, sulphurous acid, and all deoxidizing agents, speedily effect the reduction of hypermanganic acid, whether free or in combination, with formation of either peroxide or protoxide of manganese. These decompositions take place at common temperatures, in the case of the free acid as well as that of permanganates.

Permanganates are easily distinguished from all other bodies by the red colour of their solutions, by the readiness with which they decompose and lose their colour by being

3. MANGANIC ACID.—The compounds of manganic acid with bases possess an intense green colour, which they communicate to water, being very soluble in that liquid. Free manganic acid and manganates are resolved into oxygen and peroxide of manganese with greater facility than hypermanganic acid and hypermanganates, the liquid becoming colourless. Frequently, the first stage of decomposition which a manganate undergoes is resolution into a hypermanganate and peroxide of manganese, the liquid thereby changing in colour from green to crimson. Such is the immediate effect which follows the application of an acid to the green solution of a manganate; and even dilution of the green solution with water produces the same result. A solution of caustic potash is the only liquid in which manganate of potash dissolves without being converted into hypermanganate of potash.

The first effect of the application of *hydrochloric acid* to a solution of a manganate, is the production of a crimson hypermanganate; in a short time, the mixture gives off chlorine, and becomes dark brown, owing to the formation of the chloride of manganese corresponding to manganic oxide, which is decomposed immediately on the application of heat into free chlorine and the colourless protochloride of manganese.

Manganates are distinguished from all other bodies by their green colour, their convertibility by weak acids into red hypermanganates, and by their comportment with hydrochloric acid. •

CHAPTER V.

BEHAVIOUR OF NON-METALLIC ACIDS WITH REAGENTS.

SECTION I.

NON-METALLIC ACIDS PRECIPITATED FROM THEIR NEUTRAL SOLUTIONS
BY CHLORIDE OF BARIUM.

| Acids (neutralized). | Chloride of Barium. | Nitrate of Lime. | Acetate of Lead. | Nitrate of Silver. |
|---------------------------------------|---|---|---|---|
| 1. Boracic. (See also p. 121.) | A white ppt., soluble in acids, in mur. am., and much water (bo- rate of ba- rytes). | A white ppt., sol. in mur. am., and in much water (bo- rate of lime). | A white ppt., soluble in acids (bo- rate of lead). | A white ppt., soluble in acetic acid (borate of silver). |
| 2. Bromic. (See also p. 122.) | A white ppt., soluble in water (bro- mate of ba- rytes). | No ppt. | A white ppt., soluble in much wa- ter (bro- mate of lead). | A white ppt., soluble in NO_3 (bro- mate of silver). |
| 3. Carbonic. (See also p. 122.) | A white ppt. of carb. ba- rytes, sol in HCl . | A white ppt. of carb. of lime sol. in HCl . | A white ppt. of carb. of lead, sol. in NO_3 . | A white ppt., sol. in am. (carbonate of silver). |
| 4. Citric. (See also p. 123.) | A white ppt. from strong solns. (ci- trate of ba- rytes). | A white ppt., slightly sol. in wa- ter, sol. in mur. am. | A white ppt. of citrate of lead, slightly sol. in am. | A white ppt. of citrate of silver. |

| Acids (neutralized). | Chloride of Barium. | Nitrate of Lime. | Acetate of Lead. | Nitrate of Silver. |
|--|--|---|--|--|
| 5. Hydro- fluoric. (See also p. 124.) | A white ppt., sol. in HCl (fluoride of barium). | A bulky white ppt. of fluoride of calcium, nearly in- sol. in HCl. | A white ppt., soluble in HCl (flu- oride of lead). | No ppt. |
| 6. Iodic. (See also p. 125.) | A white ppt., sol. in NO_3 (iodate of barytes). | A white ppt., soluble in NO_3 (io- date of lime). | A white ppt., soluble in NO_3 (io- date of lead). | A white ppt., soluble in NO_3 and in am. (io- date of silver). |
| 7. Oxalic. (See also p. 126.) | A white ppt., nearly in- sol. in wa- ter, sol. in acids (oxa- late of ba- rytes). | A white ppt., insoluble in water, ox- alic and acetic acids, and ammoni- acal salts (oxalate of lime). | A white ppt. of oxalate of lead. | A white ppt. of oxalate of silver, soluble in NO_3 and in am. |
| 8. Phos- phoric (tribasic). (See also p. 127.) | A white ppt., soluble in HCl and slightly sol. in mur. am. (phosphate of barytes). | A white ppt., soluble in acids. Soln. of gypsum affords this ppt. | A white ppt., soluble in NO_3 nearly in- soluble in acetic acid (phosphate of lead). | A yellow ppt., sol. in NO_3 sol. in am. (phosphate of silver). |
| 9. Phos- phorous. (See also p. 128.) | A white ppt., soluble in HCl, sol. in mur. am. (phosphite of barytes). | A white ppt., soluble in NO_3 (phosphite of lime). | A white ppt., soluble in NO_3 , in- sol. in ace- tic acid. | A brown ppt. of metallic silver. |

| Acids (neutralized). | Chloride of Barium. | Nitrate of Lime. | Acetate of Lead. | Nitrate of Silver. |
|---|---|--|---|---|
| 10. Selenic. (See also p. 129.) | A white ppt., insol. in NO_5 , sol. in hot HCl . (seleniate of barytes). | A white ppt., soluble in NO_5 (se- leniate of lime). | A white ppt., insol. in NO_5 (se- leniate of lead). | A white ppt., soluble in NO_5 (se- leniate of silver). |
| 11. Silicic. (See also p. 131.) | A white ppt., sol. in di- lute HCl (silicate of barytes). | A white ppt., sol. in di- lute NO_5 , (silicate of lime). | A white ppt., soluble in NO_5 and in potash (silicate of lead). | A yellow ppt., sol. in di- lute NO_5 (silicate of silver). |
| 12. Sul- phuric. (See also p. 132.) | A white ppt. of sulphate of barytes, insol. in acids. | A white ppt. of sulphate of lime, soluble in much wa- ter. | A white ppt. of sulphate of lead, (See p. 91.) | No ppt. ex- cept in a very con- d. soln. |
| 13. Sul- phurous. (See also p. 133.) | A white ppt., soluble in HCl . | A white ppt., soluble in much wa- ter. | A white ppt., sol. in di- lute NO_5 . | A white ppt., soluble in NO_5 , and in am. |
| 14. Tarta- ric. (See also p. 134.) | A white ppt., slightly sol. in ex.; more sol. in dilute acids (tar- trate of ba- rytes). | A white ppt., almost in- sol. in wa- ter, sol. in salts of am. (tartrate of lime). | A white ppt. of tartrate of lead. | A white ppt. of tartrate of silver, sol. in am. |

ADDITIONAL OBSERVATIONS ON THE ACIDS NOTICED
IN THE PRECEDING TABLE.

The basis of the arrangement into one group of the acids mentioned in the above table, is their precipitability by chloride of barium from perfectly neutral solutions. When a solution of chloride of barium is added to a neutral liquid containing either of the above acids, a precipitate falls, consisting of a combination of barytes with the acid. But this property is possessed by several other acids; namely, those metallic acids whose characters form the subject of the two preceding chapters. All these metallic acids, however, are distinguished from the above by their precipitability by sulphuretted hydrogen, with the exception of chromic, manganic, and hypermanganic acids, the remarkable colours of whose solutions do not allow of their being confounded with either of the acids noticed in the present section.

The distribution of non-metallic acids into two classes, according to their comportment with chloride of barium, is not strictly exact; inasmuch as the saline combinations of a few acids afford precipitates with chloride of barium in concentrated, but not in moderately diluted solutions. Such is the case with hyposulphites and cyanides, the acids corresponding to which are here considered as belonging to the second section.

Some of the acids grouped together in the present section have an organic origin, namely, citric, oxalic, and tartaric; the remainder are inorganic acids, which do not blacken or carbonize on being calcined, as do most organic acids. The barytes compounds of all the acids of this class are soluble in hydrochloric acid, with the single exception of sulphate of barytes.

1. BORACIC ACID.—In the free anhydrous state, and in combination with fixed bases, boracic acid is fixed at a very intense heat, but in the presence of aqueous vapour boracic acid is slightly volatile, even below the boiling point of water. Free boracic acid is peculiar in affecting yellow turmeric paper in the manner of a free alkali; blue litmus

paper acquires a wine-red tint by free boracic acid. All borates are insoluble, with the exception of the alkaline, whose solutions are colourless, and affect test papers as a free alkali.

Free boracic acid is soluble in *alcohol*, and communicates to the flame of the latter a green tinge, most perceptible at the borders of the flame. This is the most convenient and characteristic test for free boracic acid. In the case of a borate, sulphuric acid is first applied to liberate boracic acid, the application of an excess of sulphuric acid being carefully avoided. The mixture is then evaporated to dryness, the residue mixed with alcohol, filtered, and the alcoholic liquid inflamed.

When strong *sulphuric acid* is added to a hot and concentrated solution of an alkaline borate, and the mixture allowed to become cold, scaly crystals of boracic acid are deposited.

2. BROMIC ACID.—Compounds of bromic acid with metallic oxides (bromates) are converted, by being heated to redness, into metallic bromides, with evolution of oxygen gas. If mixed with sulphur or other combustible substance, bromates detonate violently when heated; such mixtures also inflame when moistened with a drop of oil of vitriol. If mixed with oil of vitriol only, bromates disengage, without the application of heat, oxygen gas, and the vapour of bromine, which is recognized by its red colour. Bromates also afford free bromine, when mixed and heated with *hydrochloric acid* and *nitric acid*: the liberated bromine communicates a red or yellowish tinge to the solution, according to the state of dilution of the liquid.

Bromates are distinguished from all other classes of salts, except nitrites, by affording red fumes when mixed with concentrated sulphuric acid, without the application of heat. From nitrites, bromates are distinguished by being converted when heated to redness into bromides. (See the character of bromides (or hydrobromic acid) in the following section.)

3. CARBONIC ACID.—Compounds of carbonic acid with bases are recognized with great ease by the facility with which they are decomposed by dilute hydrochloric and almost all other acids, with effervescence of carbonic acid, as a

colourless and inodorous gas. In a highly dilute solution, no effervescence may occur, as free carbonic acid possesses a slight degree of solubility in cold water. In the case of alkaline carbonates, no effervescence may happen on the first addition of hydrochloric or other acid, in consequence of the formation of alkaline bicarbonates.

No carbonates except the alkaline are soluble in water which contains no free carbonic acid; but some carbonates of earthy and metallic bases are slightly soluble in water in the presence of free carbonic acid. Carbonates of earths and oxides of metals proper lose the whole or a portion of their carbonic acid when heated to redness.

Alkaline carbonates and bicarbonates affect test paper in the manner of a free alkali. In solutions of chloride of calcium and chloride of barium, alkaline carbonates produce precipitates of carbonates of lime and barytes; but alkaline bicarbonates do not, unless the mixtures are heated.

Free carbonic acid, either in the state of gas, or dissolved in water, produces, in baryta-water and lime-water, precipitates of carbonates of barytes and lime, which completely re-dissolve on applying an excess of carbonic acid. The solutions thus made become turbid when mixed with lime-water or baryta-water, and also when boiled, owing to the removal of the excess of carbonic acid and re-precipitation of the carbonate.

4. CITRIC ACID.—When heated to redness, citric acid and citrates become carbonized.

Although *chloride of calcium* and *nitrate of lime* produce a white precipitate of citrate of lime in a solution of citrate of potash or soda (see the preceding table), yet these reagents do not precipitate free citric acid from its solutions. If the solution of citrate of lime in muriate of ammonia is boiled, a dense white precipitate of basic citrate of lime is formed. Cold solutions of citric acid and citrates afford no precipitate with *lime-water*, but if the latter is in excess, a white precipitate falls when the mixture is heated; the precipitate, however, re-dissolves on cooling. If a solution of citric acid mixed with *chloride of calcium* is saturated with *ammonia*, no precipi-

tate is formed at a low temperature, unless the liquid is highly concentrated; but on boiling the mixture, a dense white precipitate of basic citrate of lime immediately appears. (Fresenius.)

Free citric acid, as well as the citrates of potash and soda (see the preceding table), produces a precipitate of citrate of lead when added to a solution of *acetate of lead*. Though only sparingly soluble in pure ammonia, this precipitate dissolves with great ease in a solution of citrate of ammonia.

Citric acid is best distinguished from the other organic acids with which it is likely to be confounded by its comportment with acetate of lead, lime-water, and chloride of calcium and ammonia.

5. HYDROFLUORIC ACID AND FLUORIDES. — Hydrofluoric acid and fluorides are detected with ease by the peculiar action of free hydrofluoric acid on siliceous substances. When this acid is placed in contact with glass or other siliceous compound, the hydrofluoric acid and silica undergo mutual decomposition, with formation of the gaseous fluoride of silicon and water: by contact with more water, fluoride of silicon affords hydrofluosilicic acid, and a deposit of silica. This property of hydrofluoric acid may be made available for the detection of fluorides in three ways:—

1. On a glass plate, thinly coated with bees' wax by warming the plate, lines are traced by means of a point of wood or ivory, so as to lay the glass bare. On this glass is placed the solution of the substance to be examined, mixed with sulphuric acid, and the mixture is allowed to become dry. If the substance under examination contained a fluoride, the glass is found, after removal of the wax, to be corroded or etched in the lines where it had been exposed.

2. The substance suspected to be a fluoride is mixed with concentrated sulphuric acid, and placed in a platinum crucible, which is covered with a glass plate prepared with wax as just described, and exposed for a quarter of an hour to a moderate heat, insufficient to melt the wax. If the substance is a fluoride, the glass is found to be etched on

the removal of the wax. The melting of the wax may be prevented in this experiment by covering the glass plate with a piece of cloth kept constantly moist with ether.

3. The substance is mixed with finely powdered glass, or siliceous sand and concentrated sulphuric acid, and the mixture is heated in a test-tube or flask, furnished with a cork and bent tube for conducting away a gas. If the substance is a fluoride, fluosilicic gas is evolved, which, when conducted into water through the bent tube, produces a gelatinous deposit of silica and an aqueous solution of hydrofluosilicic acid (see note at page 52.).

If the substance under examination is contained in solution, the first of these methods will be found most convenient; or in such a case, the liquid, mixed with sulphuric acid, may be evaporated in a glass vessel, which will of course become corroded, if a fluoride is present. The delicacy of the second of these methods is impaired by the presence of organic matters and carbonates; for which reason it is advisable, when these bodies are present, to dissolve the material in hydrochloric acid, to add excess of ammonia to the solution, and examine the precipitate thus produced, which contains all the fluoride originally present, if insoluble in water.

For a mode of detecting a fluoride when associated with a silicate, see the blowpipe test for fluorides.

6. IODIC ACID. — When strongly heated in a glass tube, free iodic acid is decomposed, being resolved into oxygen gas and free iodine. The former is recognized by its property of re-kindling a glowing match, and the latter by the beautiful violet colour of its vapour. When a neutral iodate is heated in a similar manner, oxygen gas is evolved and an iodide remains. (For the manner of detecting an iodide, see the characters of hydriodic acid, in the following section.)

When a solution of iodic acid is mixed with a *solution of sulphurous acid*, iodine is set at liberty, and the sulphurous acid becomes converted into sulphuric acid. The presence of free iodine is indicated by the production of a deep blue

compound with *starch mucilage* (see page 37.). The sulphurous acid is first applied to the solution of the substance under examination, and afterwards the starch mucilage.

By either of the characters above described, iodic acid may be distinguished from all other substances with certainty.

7. OXALIC ACID.—All oxalates are decomposed when heated to redness. Oxalates of potash, soda, lime, strontian, and barytes, disengage carbonic oxide gas at a dull red heat, and leave carbonates of the bases. Some oxalates of oxides of metals proper leave their metal in its uncombined state, and others their metallic oxide, after being heated to redness.

If heated with *concentrated sulphuric acid*, oxalic acid and dry oxalates are decomposed into carbonic acid gas and carbonic oxide gas: the former may be recognised by its property of causing a turbidity in lime-water, owing to the formation of carbonate of lime; and the latter, by its burning with a pale blue flame after having been passed through lime-water.

Lime-water, and *neutral solutions of salts of lime*, are exceedingly delicate tests for oxalic acid (see the preceding table). Even a solution of sulphate of lime is sufficiently strong to afford a white precipitate of oxalate of lime with free oxalic acid or an oxalate. Though insoluble in oxalic and acetic acids, oxalate of lime is soluble in hydrochloric and nitric acids; hence the addition of ammonia is necessary for the complete precipitation of oxalic acid by chloride of calcium or nitrate of lime, otherwise hydrochloric or nitric acid is liberated. By exposure to a dull red heat, oxalate of lime disengages carbonic oxide gas, without being blackened (if pure), and is converted into carbonate of lime. By a stronger heat, the carbonate of lime is reduced to quicklime.

The principal characters by which oxalic acid is distinguished from such bodies as are likely to be confounded with it in the course of a qualitative analysis are, 1st, its affording a white precipitate with a solution of sulphate of lime, soluble in hydrochloric acid, insoluble in acetic acid, and convertible into carbonate of lime by exposure to a red heat; and 2dly, its decomposition into carbonic oxide

and carbonic acid gases, by being heated with concentrated sulphuric acid.

8. PHOSPHORIC ACID (TRIBASIC).—No phosphates except the alkaline are freely soluble in water, but all earthy and metallic phosphates are soluble in mineral acids, though highly diluted. Even acetic acid is capable of dissolving readily several phosphates insoluble in water.

The most delicate precipitant of phosphoric acid is a *solution of a salt of magnesia*, containing some *free ammonia* or *carbonate of ammonia*. A solution of sulphate of magnesia or chloride of magnesium produces only in tolerably strong and neutral solutions of phosphates, a white precipitate of phosphate of magnesia. But if free ammonia or carbonate of ammonia is also present, and the mixture is stirred with a glass rod, a white crystalline precipitate of phosphate of magnesia and ammonia soon appears, although the solutions are highly diluted. This precipitate is insoluble in ammoniacal salts, but freely soluble in all acids.

In a salt soluble in water, phosphoric acid is also recognised by the yellow precipitate produced in its solution by nitrate of silver* (see the preceding table), and by the peculiar blow-pipe characters of the white precipitate of phosphate of lead, produced in a neutral liquid by acetate of lead. Phosphate of lead is scarcely at all reduced when heated upon charcoal in the interior flame; in the exterior flame it fuses to a colourless and transparent bead, which crystallises and becomes opaque on cooling.

In the phosphates of the alkaline earths, phosphoric acid may be detected with certainty by the following process:—To the solution of the substance in hydrochloric acid, perchloride of iron is added in excess, and afterwards a slight excess of ammonia. If any phosphoric acid is present, the precipitate consists of a mixture of phosphate of the peroxide of iron, and peroxide of iron produced from the excess of

* Solutions of *alkaline silicates* produce in a solution of nitrate of silver a precipitate which resembles the phosphate of silver, not merely in colour, but likewise in solubility in acids, and in ammonia. Before applying nitrate of silver, therefore, as the test for phosphoric acid, the absence of silicic acid should be ascertained in the usual way.

perchloride of iron. Acetic acid is added to the mixture, in order to dissolve the peroxide of iron, and the phosphate of iron which remains undissolved is collected on a filter, well washed, and then digested in hydrosulphate of ammonia, which decomposes the phosphate of iron, with formation of sulphuret of iron (insoluble) and phosphate of ammonia (soluble). The mixture is then thrown on a filter, and the filtered liquid mixed with a solution of a salt of magnesia. If phosphoric acid is present, a white precipitate of ammonio-phosphate of magnesia appears. The application of acetic acid to the mixture of oxide of iron and phosphate of iron, is not essential to this test, and need only be practised when the perchloride of iron was applied in great excess. The precipitate, however, must always be well washed before it is digested in the hydrosulphate of ammonia.

9. PHOSPHOROUS ACID. — A solution of phosphorous acid in water slowly absorbs oxygen when exposed to the air, being converted into a solution of phosphoric acid. Free phosphorous acid in a concentrated state is recognised by the decomposition it experiences at a high temperature, with evolution of phosphuretted hydrogen gas, of a very disagreeable odour, not spontaneously inflammable, but which immediately inflames on the approach of a lighted taper, giving off white fumes of phosphoric acid: when passed through a solution of nitrate of silver, this gas produces a brownish-black precipitate of metallic silver. In applying these tests, the syrupy acid may be heated in a narrow tube sealed at one end.

All phosphites are soluble in acids, but only the phosphites of the alkalis are freely soluble in water. Phosphite of lead is about the least soluble of the phosphites. Solutions of phosphites and of free phosphorous acid are powerful deoxidizing agents, owing to the disposition of phosphorous acid to pass into the state of phosphoric acid. Solutions of salts of gold afford a precipitate of metallic gold when mixed with a phosphite or phosphorous acid, at the ordinary temperature. Salts of copper are reduced by phosphites and phosphorous acid only when the mixture is boiled.

The first addition of phosphorous acid, or a phosphite, to a solution of chloride of mercury, causes the formation of a white precipitate of subchloride of mercury (calomel): when an excess of the phosphite or phosphorous acid is applied, the subchloride is further reduced to metallic mercury.

Most solid phosphites, when heated to redness, are converted into phosphates, with disengagement of hydrogen gas, which is recognised by its burning with a faint blue flame. The hydrogen is derived from the water of crystallization contained in the phosphite, the oxygen of which converts the phosphite into a phosphate. Neutral phosphites of the fixed alkalies, earths, and several metallic oxides, form neutral phosphates, when thus heated. Other phosphites, containing but little water, among which is the phosphite of lead, become converted into basic phosphates, with disengagement of a mixture of hydrogen gas and phosphuretted hydrogen gas, not spontaneously inflammable. (Rose.) In applying this character as a test, the material may be heated in a narrow glass tube sealed at one end.

The only acid with which phosphorous acid is easily confounded, after the application of the above tests, is hypophosphorous acid. The latter likewise reduces several metallic salts, and disengages phosphuretted hydrogen gas when strongly heated in the free state. To distinguish these bodies, the acid is carefully neutralised with potash, soda, or barytes, the liquid is evaporated to dryness, and the dry residue is strongly heated in a narrow glass tube-retort. A hypophosphite then disengages phosphuretted hydrogen gas, spontaneously inflammable, producing in its combustion dense white fumes of phosphoric acid. A phosphite, on the other hand, disengages hydrogen gas, which burns on the approach of a lighted taper, with a blue flame, without white fumes. All compounds of hypophosphorous acid with bases are soluble in water, but many phosphites of oxides of metals proper are nearly insoluble in water. (See page 128.)

10. SELENIC ACID.—The compounds of bases with selenic acid possess considerable resemblance to the analogous compounds of sulphuric acid; hence, selenic and sulphuric

acids may be confounded in the course of a qualitative analysis. The seleniates of lime, barytes, strontian, and oxide of lead, for example, are insoluble, or but slightly soluble, in water and cold diluted acids, as the corresponding sulphates. Seleniate of barytes is distinguished from sulphate of barytes by being soluble, with decomposition, in boiling hydrochloric acid. Pure hydrated selenic acid is a colourless liquid, of an oleaginous consistence, which decomposes, when heated above 550° Fahr., into oxygen gas and selenious acid.

When boiled with *hydrochloric acid*, selenic acid is decomposed, whether in the free state, or in combination with bases: the selenic acid becomes converted, in this case, into selenious acid, a part of its oxygen uniting with the hydrogen of the hydrochloric acid to form water, and the chlorine of the hydrochloric acid being liberated. After expulsion of the free chlorine by ebullition, the solution comports with reagents as pure selenious acid (see pages 102. and 111.), giving precipitates with sulphuretted hydrogen and sulphurous acid; but neither of these produces any precipitate in a pure solution of selenic acid. Owing to the presence of free chlorine, the mixture of selenic and hydrochloric acids possesses the power of dissolving metallic gold and platinum.

When a mixture of a seleniate with *sal-ammoniac* is heated in a glass tube, selenium rises in vapour, and condenses on the cool part of the tube.

Selenic acid is distinguished from all other acids, except sulphuric, by its property of forming, with a solution of a barytes salt, a white precipitate of seleniate of barytes, insoluble in nitric acid: this precipitate is distinguished from sulphate of barytes by its solubility in boiling hydrochloric acid. The conversion of selenic acid and seleniates, when boiled with hydrochloric acid, into selenious acid and selenites, with disengagement of free chlorine, presents the most decisive test for these bodies. The free chlorine is recognised by its odour and bleaching action on organic colouring matters, and the selenious acid by the tests mentioned at page 111.

11. **SILICIC ACID.**—Silicic acid is met with in two states, one of which is soluble in acids and in water; but the other is insoluble in all acids except hydrofluoric. In either of these states, silicic acid is soluble in a boiling solution of potash, but the soluble modification dissolves in potash much more freely than the insoluble. When the soluble silicic acid is heated, no free alkaline or earthy base being present, it is converted into insoluble silicic acid, being no longer soluble in hydrochloric acid.

When insoluble silicic acid is fused with potash or soda, or their carbonates, an alkaline silicate is formed, which dissolves in water. If insoluble silicic acid is heated to bright redness with caustic barytes or quicklime, a silicate of barytes or lime is formed, nearly insoluble in water, but soluble in hydrochloric acid. The only silicates which dissolve freely in water are those having an alkaline base.

As *free* silicic acid occurs in two states, the one soluble, the other insoluble in hydrochloric acid, so *silicates of bases* are found in two states, soluble and insoluble in hydrochloric acid. If an insoluble silicate is heated to redness in contact an alkali, an alkaline carbonate, caustic barytes, or quicklime, the silicic acid is converted into the soluble modification.

When a soluble silicate is mixed with hydrochloric acid, it is decomposed, a chloride of the base being formed, and silicic acid set at liberty. If the proportion of hydrochloric acid present is small, a portion of the silicic acid may remain undissolved, in the form of a transparent jelly; but if the proportion of silicic acid is small, it may be completely dissolved by hydrochloric acid. When a solution of silicic acid in hydrochloric acid is evaporated, and the residue heated until it is perfectly dry, the silicic acid passes from the soluble to the insoluble form; so that when the residue of the evaporation is treated with water or hydrochloric acid, the chloride which may happen to be mixed with silicic acid dissolves, and leaves the silicic acid wholly undissolved.

In testing any substance whatever for silicic acid, it is mixed with hydrochloric acid, (after fusion with an alkaline

carbonate, when the substance is not attacked by hydrochloric acid without,) the mixture is evaporated to dryness, and the dry residue treated with dilute hydrochloric acid. Silicic acid, if present, remains undissolved. The residue should be further examined before the blowpipe. (See the blowpipe characters of silicic acid.)

12. SULPHURIC ACID. — Sulphuric acid is recognised with ease in its soluble combinations, by affording, with a solution of a *barytes salt*, a white precipitate of sulphate of barytes, insoluble in all acids. A solution of selenic acid produces, with barytes solutions, a white precipitate of seleniate of barytes, insoluble in nitric acid: but the seleniate is distinguished from sulphate of barytes by its solubility in boiling hydrochloric acid, with disengagement of free chlorine. (page 130.)

If a solution of chloride of barium or nitrate of barytes is mixed with a liquid containing much free hydrochloric or nitric acid, a precipitate of chloride of barium, or nitrate of barytes, may be produced, and an erroneous conclusion be drawn concerning the presence of sulphuric acid. The precipitation of these salts is owing to their smaller degree of solubility in the above acids than in water. On diluting the mixture with water they immediately dissolve, whereby they are distinguished from sulphate of barytes. The first addition of a solution of chloride of barium to a mixture of nitric acid with a little sulphuric acid, causes the precipitation of nitrate of barytes, instead of sulphate of barytes; for if the acid liquid is poured off from the precipitate, and the latter washed with pure nitric acid, it may be completely dissolved in distilled water.

To detect sulphuric acid in sulphates insoluble or but slightly soluble in water and dilute acids, (sulphates of lime, barytes, strontian, and lead,) the sulphate is boiled for some time in a solution of carbonate of soda, whereby sulphate of soda and an insoluble carbonate of the base are formed. The liquid is filtered, supersaturated with hydrochloric acid, and tested for sulphuric acid with chloride of barium.

Hydrofluosilicic acid produces, in solutions of barytes salts,

a white precipitate of fluosilicate of barytes, which resembles sulphate of barytes in being nearly insoluble in nitric and hydrochloric acids. But hydrofluosilicic acid may be distinguished from sulphuric acid by not producing any precipitate in solutions of salt of lead and strontian, as sulphuric acid does; and fluosilicate of barytes does not behave like sulphate of barytes when heated with soda in the reducing flame of the blowpipe. (See the characters of sulphates before the blowpipe, in the chapter on Blowpipe Analysis.)

13. **SULPHUROUS ACID.**—Sulphurous acid in the free state, and unmixed with other volatile acids, is readily recognised by its peculiar and highly pungent odour.* Sulphurous acid gas, and the aqueous solution of sulphurous acid, destroy the colour of paper stained with an infusion of Brazil wood. By exposure to air, a solution of sulphurous acid gradually absorbs oxygen, loses its odour, and becomes a solution of sulphuric acid.

Nitric acid and oxidizing agents in general, convert sulphurous acid into sulphuric acid. When *iodic acid* is mixed with sulphurous acid, iodine is set at liberty, in consequence of the complete deoxidation of the iodic acid. The liberated iodine is detected by starch mucilage (page 148.), which forms a blue compound with iodine. (See the mode of detecting sulphurous acid in hydrochloric acid by this test, described at page 19.) If a liquid contains sulphuric acid after the application of chlorine or pure nitric acid, but none before, the presence of sulphurous acid may be inferred. To apply this test, the liquid is mixed first with a solution of chloride of barium, and afterwards, if a precipitate is produced, with pure hydrochloric acid and water, to ascertain whether the precipitate is entirely soluble in that acid, in which case no sulphuric acid is present. On adding a little nitric acid to the hydrochloric solution, a white precipitate of sulphate of barytes is soon produced, if the liquid contained sulphurous acid. If chloride of barium produces in the original liquid a precipitate of sulphate of barytes, insoluble in hydrochloric

* The suffocating vapour which rises from burning sulphur is sulphurous acid gas.

acid and water, the hydrochloric solution may be filtered and tested for sulphurous acid by nitric acid, as if no sulphuric acid was present.

Neutral solutions of *sulphites* do not exhale the odour of sulphurous acid, but if *sulphuric* or *hydrochloric acid* is mixed with a sulphite, free sulphurous acid is immediately disengaged without any precipitation of sulphur.* From a very concentrated solution of a sulphite, sulphurous acid is evolved with effervescence.

Sulphurous acid precipitates metallic gold from a solution of *chloride of gold* without the application of heat. (page 89.) Salts of silver and some other metals are also reduced by sulphurous acid, but very slowly without the assistance of heat.

14. TARTARIC ACID.—When heated to redness, tartaric acid, and compounds of tartaric acid with bases, become carbonized, and disengage at the same time a peculiar odour, by which they may be distinguished from most other bodies which carbonize when ignited.

When a solution of a *salt of potash* is mixed with free tartaric acid, a white crystalline precipitate of bitartrate of potash (cream of tartar) appears, sparingly soluble in water, but freely soluble in alkalies and mineral acids. Bitartrate of potash is considerably less soluble in an alcoholic liquid than in water, and its solubility is not increased by free acetic acid; therefore the best way of applying a salt of potash as a test for free tartaric acid, is to use the *acetate of potash* as the precipitant, and to add some alcohol to the mixture. Stirring with a glass rod accelerates the precipitation of bitartrate of potash.

If a neutral solution is to be tested for tartaric acid, free acetic acid may first be applied, and afterwards a solution of acetate of potash with some alcohol.

The only substance with which tartaric acid is likely to be confounded, in the course of a qualitative analysis, is racemic

* The property of disengaging sulphurous acid, and affording at the same time a milk-white precipitate of sulphur when mixed with hydrochloric or sulphuric acid, is characteristic of the class of salts termed hyposulphites.

or paratartaric acid. Tartaric and racemic acids resemble each other, and differ from other acids, in being precipitated by a solution of a salt of potash, in disengaging a peculiar odour when carbonized, and by affording white precipitates with lime-water in excess, which are soluble in a solution of potash in the cold, but not when heat is applied.* Tartaric and racemic acids may be distinguished from each other by the following characters. The precipitate of tartrate of lime, produced on adding *lime-water* in excess to tartaric acid, is very soluble both in *solution of tartaric acid* and in *solution of muriate of ammonia*; but the precipitate of racemate of lime, formed on mixing lime-water with racemic acid, is insoluble both in solution of tartaric acid, and in solution of ammonia. Solution of *sulphate of lime* produces, in a solution of free racemic acid, a white precipitate of racemate of lime, after the lapse of about a quarter of an hour; but free tartaric acid affords no precipitate with a solution of sulphate of lime. Neutral solutions of racemates with the same reagent yield a precipitate immediately, but solutions of neutral tartrates only after some time, and then a scanty one. (Fresenius.)

SECTION II.

NON-METALLIC ACIDS NOT PRECIPITATED FROM THEIR SOLUTIONS BY CHLORIDE OF BARIUM.

| Acids (neutralized). | Nitrate of Lime. | Acetate of Lead. | Nitrate of Silver. |
|-------------------------------------|------------------|------------------|--|
| 1. Acetic. (See also p. 138.) | No ppt. | No ppt. | From concd. solns., a cryst. ppt. of acetate of silver. |

* When the solution of tartrate or racemate of lime in solution of potash is boiled, it becomes turbid, owing to the precipitation of the tartrate or racemate of lime; but as the liquid cools, the precipitate redissolves, and the solution again becomes clear.

| Acids (neutralized). | Nitrate of Lime. | Acetate of Lead. | Nitrate of Silver. |
|---|------------------|--|---|
| 2. Chloric. (See also p. 138.) | No ppt. | No ppt. | No ppt. |
| 3. Formic. (See also p. 139.) | No ppt. | No ppt. except in very strong solutions. | If the mixture is heated slowly, a black powder of metallic silver appears. |
| 4. Hydro- chloric. (See also p. 140.) | No ppt. | A white ppt. slightly sol. in water (chloride of lead). | A curdy white ppt., insol. in NO_3 , sol. in am. (chloride of silver). |
| 5. Hydro- cyanic. (See also p. 142.) | No ppt. | A white ppt. of cyanide of lead. | A white ppt., insol. in dilute NO_3 , sol. in am. and in cyanide of potm. (cyanide of silver). |
| 6. Hydro- bromic. (See also p. 145.) | No ppt. | A white ppt., sol. in NO_3 (bromide of lead). | A yellowish ppt., insol. in dilute NO_3 , slightly sol. in am. (bromide of silver). |
| 7. Hydro- iodic. (See also p. 146.) | No ppt. | A yellow ppt., sol. in NO_3 , and in hot water. It becomes whitish with excess of acct. lead. | A yellowish ppt., insol. in NO_3 , nearly insol. in am. (iodide of silver). |

| Acids (neutralized). | Nitrate of Lime. | Acetate of Lead. | Nitrate of Silver. |
|---|------------------|---|--|
| 8. Hydro-selenic. (See also p. 149.) | No ppt. | A black ppt. of seleniuret of lead. | A black ppt. |
| 9. Hydrosulphocyanic. (See also p. 149.) | No ppt. | No ppt. if the solutions are moderately dilute. | A curdy white ppt., sol. in strong but not in dilute am. |
| 10. Hydrosulphuric. (See also p. 150.) | No ppt. | A black ppt. of sulphuret of lead. | A black ppt., insol. in am. (sulphuret of silver). |
| 11. Hypo-sulphuric. (See also p. 151.) | No ppt. | No ppt. | No ppt. |
| 12. Hyposulphurous. (See also p. 153.) | No ppt. | A white ppt., slightly sol. in NO_3 . | A white ppt., becoming black. |
| 13. Nitric. (See also p. 154.) | No ppt. | No ppt. | No ppt. |
| 14. Nitrous. (See also p. 156.) | No ppt. | No ppt. | A white ppt., slightly sol. in water. |
| 15. Perchloric. (See also p. 157.) | No ppt. | No ppt. | No ppt. |

ADDITIONAL OBSERVATIONS ON THE CHARACTERS OF THE ACIDS NOT PRECIPITATED BY CHLORIDE OF BARIUM.

1. ACETIC ACID. — Free acetic acid volatilizes without residue when heated, affording vapours of a peculiar and pungent odour. Acetates evolve the same odour when moistened with concentrated *sulphuric acid*, owing to the liberation of acetic acid. If about equal weights of *oil of vitriol* and *alcohol* are mixed with an acetate, and the mixture heated, the characteristic odour of acetic ether is evolved. This character may be conveniently applied as a satisfactory test for an acetate. Nearly all acetates are freely soluble in water: the acetates of silver and suboxide of mercury are about the least soluble of this class of salts. All acetates are decomposed by being heated to redness.

The most decisive test for acetic acid is founded on the property which this acid possesses of dissolving an excess of *protoxide of lead* (litharge); thus forming a solution which produces an alkaline reaction on test paper. This property is possessed by no volatile organic acid except acetic acid. In testing after this manner for acetic acid in combination with a base, the substance is mixed with sulphuric acid, the mixture distilled, the product of distillation mixed with litharge in excess, and after a little while, tested with red litmus paper. If the paper is rendered blue, acetic acid is present.

Nitrate of silver does not produce in free acetic acid a precipitate of acetate of silver, as the same reagent does in a strong solution of a neutral acetate. (See the preceding Table.)

2. CHLORIC ACID. — All compounds of chloric acid with bases are soluble in water: the least soluble of this class of bodies is the chlorate of potash. Free chloric acid is a very unstable substance, being decomposed, when its solution is evaporated at a moderate heat, into free chlorine and perchloric acid. Free chloric acid, but not a chlorate, bleaches vegetable colouring matters: hence one test for a chlorate consists in adding to the neutral solution, first, a dilute

solution of sulphate of indigo, and then sulphuric acid. If the blue tint disappears on the addition of the sulphuric acid, but not before, the presence of either a chlorate or a nitrate may be inferred.

When heated to redness, chlorates are converted into chlorides, all their oxygen being disengaged. The presence of a chloride in the calcined substance is detected by nitrate of silver. To observe whether oxygen gas is evolved during calcination, the substance is heated in a narrow glass tube, sealed at one end, and somewhat contracted at the other: on introducing a glowing match into the tube, the match is rekindled, if much oxygen gas is disengaged.

When a dry chlorate is mixed with sulphur, charcoal, sugar, or other like combustible substance, and the mixture heated, a very violent deflagration or detonation occurs: with sulphur, mere friction or percussion causes a detonation; and when such a mixture is touched with a drop of concentrated sulphuric acid, it immediately bursts out into flame. Very minute quantities of the materials should be operated on, in such experiments, particularly when phosphorus is used.

When heated with excess of *hydrochloric acid*, chlorates are decomposed, with formation of free chlorine, which is recognised by its odour and bleaching action on vegetable colouring-matters; and, if in the state of gas, by its yellow colour. When moistened with *concentrated sulphuric acid*, chlorates disengage chlorous acid, as a greenish-yellow gas of a peculiar odour, and are converted into perchlorates. To prevent chance of explosion, in this experiment, small quantities of materials should be operated on, and the application of heat carefully avoided.

3. FORMIC ACID.—The only acid with which formic acid is easily confounded is acetic acid. Both formic and acetic acids are volatile, and disengage a pungent acid vapour, which is inflammable when produced from the concentrated acid: formiates and acetates also give rise to similar products when subject to destructive distillation; and cold strong solutions of formiates and acetates produce, *at first*, similar

white precipitates in cold solutions of nitrate of silver and protonitrate of mercury.

The principal peculiarities of formic acid are the two following:—

1st. If the white precipitates produced by a formiate in tolerably strong solutions of nitrate of silver and protonitrate of mercury are allowed to stand, they gradually become black, owing to the separation, from these precipitates, of metallic silver and metallic mercury, through the deoxidizing power of formic acid, which becomes converted into carbonic acid and water. The production of metallic silver or mercury is almost instantaneous, if the mixture of the formiate with the metallic solution is heated, even though the solutions are not strong enough for the production of a white precipitate in the cold. When a solution of corrosive sublimate is gently heated with formic acid, a precipitate of calomel is formed; but at the boiling point, the precipitate consists of metallic mercury.

2nd. When a formiate is heated with oil of vitriol, it is decomposed without being blackened, and carbonic oxide gas is disengaged, which takes fire on the approach of a lighted taper, giving a pale blue flame, without smoke. The carbonic oxide thus produced is unaccompanied by carbonic acid, as happens when an oxalate or oxalic acid is decomposed by oil of vitriol in like manner. (page 126.)

4. HYDROCHLORIC ACID AND CHLORIDES. — Hydrochloric acid, in the free state, is a colourless gas, which is absorbed by water with remarkable avidity. When the pure dry gas, or the vapour which arises from the aqueous solution of this acid, is brought into contact with ammonia, dense white fumes are produced, consisting of muriate of ammonia. When mixed with a metallic oxide (a base), hydrochloric acid gives rise to the formation of water and a metallic chloride. All chlorides which are not decomposed by water, dissolve freely in that liquid, with the exception of chloride of silver, chloride of lead, and subchloride of mercury (calomel).

When *nitric acid*, is added to hydrochloric acid, nitro-

muratic acid or aqua regia is formed. Aqua regia contains free chlorine (see page 21.), and consequently possesses the power of dissolving gold, though this property is possessed by neither nitric nor hydrochloric acid separately. Other bodies besides hydrochloric acid, form with nitric acid a mixture which dissolves gold: hence this character cannot be applied as a conclusive test for hydrochloric acid.

Nearly all chlorides, when gently warmed with *concentrated sulphuric acid*, disengage hydrochloric acid as a colourless gas, which produces dense white fumes on the approach of a rod moistened with some strong solution of ammonia. In this experiment, the chloride becomes converted into a sulphate. The two chlorides of mercury, and the two chlorides of tin, do not disengage hydrochloric acid when heated with sulphuric acid.

When hydrochloric acid is heated with *peroxide of manganese*, and when a chloride is heated with *sulphuric acid* and *peroxide of manganese*, chlorine gas is evolved, which is recognised by its odour, its yellow colour, and its bleaching action on litmus paper and all vegetable colouring-matters.

A solution of *nitrate of silver*, or any other soluble salt of silver, is an extremely delicate test for hydrochloric acid and chlorides. (See the preceding Table.) By the insolubility of the precipitated chloride of silver in hot nitric acid, hydrochloric acid may be distinguished from all other acids except hydrobromic, hydriodic, hydrocyanic, and bromic. Chloride of silver is quite white when first precipitated, but soon becomes grey on exposure to light; when heated to a temperature below redness, it fuses without decomposition, and remains transparent when again cooled, by which character chloride of silver is distinguished from cyanide of silver (see page 142.); its easy solubility in ammonia distinguishes chloride from iodide of silver; and its not detonating when heated with combustibles, distinguishes it from the bromate of silver.

For the detection of a chloride, in a substance which also contains a bromide, the application of the following character has been recommended. (M. Fresenius.) If a chloride is well

mixed with some *chromate of potash*, and sufficient *strong sulphuric acid* to moisten the mass thoroughly, and the mixture heated in a little retort, a deep brownish-red vapour of chromate of perchloride of chromium is disengaged, which, condenses in the receiver as a liquid of the same colour. When this liquid is mixed with solution of ammonia in excess, a yellow solution of chromate of ammonia is obtained, which becomes reddish-yellow on being mixed with an acid, through the formation of bichromate of ammonia. When a bromide is treated in the same manner, a brownish-red liquid also distils over into the receiver; but this consists of bromine, and becomes colourless, instead of yellow, when mixed with excess of ammonia.*

5. HYDROCYANIC ACID AND CYANIDES.—Hydrocyanic acid, in a state of purity, is a colourless liquid, miscible with water in all proportions, entirely volatile, and possessed of a very strong and peculiar odour.

Several cyanides of heavy metals, among which are the cyanides of silver and mercury, are stable compounds, being scarcely at all acted on by diluted sulphuric and nitric acids: most of them, however, are completely decomposed by sulphuretted hydrogen and by hydrochloric acid. When such cyanides are heated to redness, they are decomposed; some being resolved into cyanogen gas and metals, and others into nitrogen gas and carburets of metals.

The cyanides of alkaline metals, and of the metals of the alkaline earths, on the contrary, are decomposed by acids with great facility when in aqueous solution; even by the carbonic acid of the air; but when heated to redness, without access of air, such cyanides undergo no alteration.

Free hydrocyanic acid, as well as solutions of cyanides, afford, with *nitrate of silver*, a white precipitate of cyanide of silver. (See the preceding Table.) When heated to redness, this precipitate disengages cyanogen gas, and metallic silver remains behind. Cyanide of silver is scarcely at all soluble in hydrocyanic acid; it dissolves to a small extent in a strong, but not in a dilute, solution of nitrate of silver, and is very

* Fresenius's Elementary Instruction in Chemical Analysis, pages 148, 150.

soluble in solutions of alkaline cyanides. From its solution in an alkaline cyanide, cyanide of silver is precipitated by dilute nitric acid.

When a *mixture of a salt of the protoxide of iron and a salt of the peroxide of iron** is added to a solution of an alkaline cyanide, a precipitate of prussian blue is produced. This reaction does not take place with free hydrocyanic acid: for the detection of the latter, therefore, in this manner, an alkali must be applied, in order to produce an alkaline cyanide. This addition of the alkali may either precede or follow the application of the salt of iron. As both the alkali and the salt of iron are usually applied in large excess, the precipitate formed by the alkali may consist merely of oxide of iron, the prussian blue at first precipitated being redissolved by the excess of alkali. By next applying, however, an excess of hydrochloric acid, the oxide of iron is dissolved, and prussian blue alone remains undissolved. For the detection of free hydrocyanic acid, therefore, there should be applied—1°, a little caustic potash; 2°, a solution of copperas which has been exposed to the air for some time; and, 3°, after agitation, an *excess* of hydrochloric acid. If a blue precipitate remains undissolved, the presence of hydrocyanic acid may be inferred with certainty. This excellent test for hydrocyanic acid is distinguished as Scheele's test.

When hydrocyanic acid is mixed with a solution of the *nitrate of the suboxide of mercury*, metallic mercury is precipitated, and cyanide of mercury remains in solution.

Free hydrocyanic acid and a solution of cyanide of potassium (although mixed with caustic potash) dissolve finely powdered *red oxide of mercury* with ease. It is said that no alkaline liquid but such as contains a cyanide is capable of dissolving the red oxide of mercury.

To detect cyanogen in the cyanides of metals proper which are decomposed by sulphuretted hydrogen, in the presence of water, as the cyanides of lead, silver, and mercury †, these

* A solution of copperas which has been exposed to the air for some time contains sufficient peroxide of iron to be employed in this experiment.

† Although cyanide of mercury is soluble, yet its cyanogen cannot be detected by Scheele's test, at least when performed in the ordinary way. The

bodies are mixed with water, and exposed to sulphuretted hydrogen, whereby the sulphurets of the respective metals and free hydrocyanic acid are produced: the latter may be detected in the liquid, after filtration, by Scheele's test, or (if there is no excess of sulphuretted hydrogen present) by its solvent power on red oxide of mercury, whether mixed with an excess of alkali or not.

Cyanogen unites with iron, cobalt, chromium, and some other metals, to form compounds which stand in the relation to metals of a salt-radical; being capable of uniting with metals to form true salts, and with hydrogen to form true acids. The cyanogen in such combinations cannot be detected by the ordinary tests for that body. The most important classes of salts formed by the union of such compound radicals with metallic bases are the ferrocyanides and ferridecyanides. Their corresponding acids are called hydroferrocyanic and hydroferridecyanic acids. The common yellow prussiate of potash (page 29.) is the ferrocyanide of potassium; and the red prussiate of potash (page 30.) is the ferridecyanide of potassium.

The soluble *ferrocyanides* are recognised by affording with a solution of a salt of the *peroxide of iron* a precipitate of prussian blue, insoluble in hydrochloric acid; and with a solution of *sulphate of copper* a chocolate-brown precipitate of ferrocyanide of copper. With a solution of a salt of *protoxide of iron*, a ferrocyanide affords a white or blueish-white precipitate, which gradually becomes more blue on exposure to the air. When insoluble ferrocyanides are digested in a solution of caustic potash, the base of the ferrocyanide is separated as an oxide, and ferrocyanide of potassium is formed.

following mode of applying Scheele's test to the detection of cyanogen in cyanide of mercury has been pointed out by M. Fresenius. The solution of cyanide of mercury is mixed with hydrochloric acid and metallic iron, upon which metallic mercury is precipitated, and a solution of hydrocyanic acid and protochloride of iron formed. A portion of the latter, when the excess of metallic iron is removed, absorbs oxygen from the air, and gives rise to a salt of the peroxide of iron. On the addition, then, of an excess of alkali, yellow prussiate of potash is formed, and oxide of iron precipitated: the latter is lastly dissolved by applying an excess of hydrochloric acid, when the prussian blue appears of its proper colour.

The soluble *ferridcyanides* are distinguished by affording a precipitate of prussian blue with a solution of a salt of *protoxide of iron*; with a solution of a salt of peroxide of iron, they yield no precipitate. Insoluble ferridcyanides are decomposed by caustic potash in the same manner as insoluble ferrocyanides.

When heated with sulphuric acid, ferrocyanides and ferridcyanides afford free hydrocyanic acid, which may be distilled over and collected in a receiver.

6. HYDROBROMIC ACID AND BROMIDES. — Pure hydrobromic acid is a colourless gas, possessed of great solubility in water, forming a colourless solution. When hydrobromic acid gas is allowed to escape into the air, it produces white fumes, through condensing with the aqueous vapour in the air. In their general characters, hydrobromic acid gas, the aqueous solution of hydrobromic acid, and the bromides, possess considerable resemblance to hydrochloric acid and chlorides.

A solution of free hydrobromic acid, as well as of a bromide, is precipitated by *nitrate of silver*. (See the preceding Table.) The precipitate of bromide of silver is distinguished from chloride of silver, — 1st, by its feeble yellow tint, which disappears on the addition of hydrochloric acid, owing to the conversion of the bromide into chloride of silver; and, 2nd, by affording, when mixed with hydrochloric acid and chloride of lime (bleaching powder), a reddish or yellow liquid containing free bromine, which, if concentrated, disengages ruddy fumes of bromine on being heated.

When hydrobromic acid, or a bromide, is placed in contact with a powerful oxidizing agent, as *free chlorine* or *hot nitric acid**, the mixture becomes yellow or yellowish-red (according to its state of concentration), owing to the liberation of bromine. If such a mixture is heated, the free bromine passes off in the state of ruddy fumes, which may be condensed in drops of the same colour. Free hydrobromic acid is decom-

* Cold nitric acid is nearly without action on bromides.

posed in this manner, when warmed with *bleaching powder*, and with *peroxide of manganese*; and soluble bromides, when warmed with both *sulphuric acid* and *peroxide of manganese*, and also with a mixture of *hydrochloric acid* and *bleaching powder*.

To distinguish a bromide from a chloride, or hydrobromic acid from hydrochloric acid, the solution of the substance may either be exposed to a little gaseous chlorine or be mixed with an aqueous solution of chlorine, and afterwards agitated with some ether (sulphuric ether). After agitation, the ether rises to the surface, possessed of a yellow or reddish colour when bromine is present, having abstracted from the aqueous solution all the bromine liberated by the chlorine. When the yellow ethereal solution is mixed with a little caustic potash and evaporated to dryness, and the residue heated to redness, bromide of potassium remains, mixed with the excess of caustic potash. This residue may be heated in a tube with sulphuric acid and peroxide of manganese, in order to observe the reddish fumes of bromine.

Solutions of free bromine and free iodine resemble each other in their colour, but these elements are readily distinguished by their action on *gelatinous starch*, which is rendered yellow by free bromine, but deep blue by free iodine. The yellow colour of the compound of starch and bromine slowly disappears on exposure to the air.

A solution of *chloride of gold* has been suggested as a test for hydrobromic acid and alkaline bromides, from its property of producing a red tinge when mixed with solutions of these bodies. (Dr. G. Wilson.)

(For a method of distinguishing between a chloride and a bromide by means of chromate of potash, see page 142.)

7. HYDRIODIC ACID AND IODIDES. — The physical properties of hydriodic acid and soluble iodides bear considerable resemblance to those of hydrochloric acid and soluble chlorides, and hydrobromic acid and soluble bromides. Iodides which are insoluble in water, frequently differ from the corresponding chlorides in the possession of striking colours. Those

iodides which are insoluble in water dissolve to a greater or less extent in a solution of iodide of potassium.

Hydriodic acid and soluble iodides are decomposed by several *oxidizing agents*, in the same manner as hydrobromic acid and bromides, iodine being set at liberty. The free iodine communicates a yellow or brown colour to the solution, according to the degree of concentration of the liquid. When such a solution of free iodine is heated, the iodine volatilizes completely, in the form of a purple vapour, unless the proportion of iodine present is very minute, when the colour of the vapour is scarcely perceptible. Iodine condenses from its vapour in crystalline spangles, almost black. When a solution of hydriodic acid is exposed to the *air*, oxygen is absorbed, and the hydriodic acid decomposed, water being formed and iodine liberated. Solutions of iodides, when mixed with sulphuric or hydrochloric acid, and exposed to the air, become brown from the same cause. *Chlorine* and *nitric acid* immediately liberate iodine from hydriodic acid and soluble iodides, even at ordinary temperatures. If chlorine is applied in excess, it enters into combination with the liberated iodine, and the yellow or brown colour developed by the first application of chlorine disappears, the compound of chlorine and iodine being colourless. Iodine is also liberated when an iodide is heated with *sulphuric acid* and *peroxide of manganese*, or even with *strong sulphuric acid* only; in the latter case, sulphurous acid gas is also evolved.

The precipitate of iodide of silver produced by *nitrate of silver* in a solution of hydriodic acid, or of an alkaline iodide (see the preceding Table), is distinguished from chloride of silver by its yellowish tint, and by its very slight degree of solubility in ammonia. Iodide of silver blackens on exposure to light; it is not decomposed by exposure to a red heat.

When a solution of *protoxide of copper* (black oxide) is mixed with a solution of an iodide, a whitish precipitate of subiodide of copper is formed, and the solution contains free iodine. But if *sulphurous acid* or a salt of the *protoxide of iron* is also present, the whole of the iodine may be precipitated as subiodide of copper. A convenient solution for this

purpose is made by dissolving in water one part of crystallized sulphate of copper, and two parts and a quarter of copperas. This solution does not precipitate chlorides or bromides, and therefore affords one method of distinguishing those salts from iodides.

When *starch mucilage* (see page 37.) is added to a *cold* solution containing *free* iodine, a blue colour immediately appears, owing to the formation of a deep blue compound of starch and iodine. If the iodine is present in tolerable quantity, the colour is so deep as to appear quite black, and the iodide of starch may be precipitated. To produce this blue compound with starch, iodine must exist in the free state; therefore hydriodic acid and solutions of iodides are not at all affected by the application of starch. But if an oxidizing agent, such as nitric acid or chlorine, is applied to a mixture of an iodide with starch, iodine is immediately set at liberty, and its characteristic comportment with starch exhibited. Nitric acid is generally a more convenient means of oxidation in such a case than chlorine, as the latter, if applied in excess, would prevent the action of iodine on the starch, by giving rise to the formation of the chloride of iodine. A large excess of nitric acid also causes the blue colour of iodide of starch to disappear; therefore that acid should be added by single drops to the cold mixture of starch mucilage with the solution suspected to contain an iodide.* Chlorine is conveniently applied in the form of chlorine water, added in very minute quantities at a time; or a little chlorine gas may be allowed to fall upon the surface of the mixture of starch with the liquid under examination, from a jar of chlorine water, held above the mixture in an inclined position, without any of the chlorine water being poured out. If chlorine has been applied in excess, so as to destroy the blue colour at first produced, the blue colour may be restored by the introduction of a reducing agent, as protochloride of tin. The blue colour of iodide of starch disappears on the application of

* It is said that by the test of nitric acid and starch, carefully applied, an alkaline iodide may be detected in a solution in which it is contained in so small a proportion as one part in 4,000,000.

heat, of a caustic alkali, and some deoxidizing agents, as phosphorous acid and sulphurous acid, as well as by an excess of chlorine and nitric acid. The presence of arsenious acid interferes with the starch test for an iodide when chlorine is employed to liberate the iodine, but not when nitric acid is used for that purpose. (Rose.) It is also to be observed, that starch does not detect iodine in a solution of chloride of mercury containing iodide of mercury. *Protochloride of palladium* has recently been recommended as an exceedingly delicate test for a soluble iodide. A solution of this reagent produces a black precipitate of protiodide of palladium in solutions of alkaline iodides. (M. Lassaigne.) Bromides afford no precipitate with this reagent.

8. HYDROSELENIC ACID AND SELENIURETS. — Hydroselenic acid, also called seleniuretted hydrogen, is a colourless gas, slightly soluble in water, and possessed of an extremely disagreeable odour, similar to that of sulphuretted hydrogen. It is poisonous in a very high degree. When exposed to the air in solution it is decomposed, oxygen being absorbed, water formed, and selenium set at liberty. The latter communicates a reddish colour to the solution. Seleniuretted hydrogen precipitates several metals from their solutions as seleniurets, in like manner as sulphuretted hydrogen precipitates the same metals as sulphurets. The precipitated seleniurets in general resemble the corresponding sulphurets in physical and chemical properties. The blowpipe affords a ready and certain means of detecting metallic seleniurets. (See the chapter on Blowpipe Analysis.)

9. HYDROSULPHOCYANIC ACID AND SULPHOCYANIDES. — Free hydrosulphocyanic acid is miscible with water in all proportions, forming a solution which possesses a strong acid taste. The concentrated acid has a pungent odour, but not similar to that of hydrocyanic acid.

Soluble sulphocyanides are recognised by their property of striking a deep blood-red colour with a solution of a *salt of the peroxide of iron*, without the formation of a precipitate. Solutions of protoxide of iron do not afford a red liquid with a solution of a sulphocyanide. The red colour of a liquid

containing a sulphocyanide and peroxide of iron is destroyed by the introduction of iron filings, ammonia, corrosive sublimate, protochloride of tin, sulphuretted hydrogen, and oxalic, iodic, phosphoric, and arsenic acids.

By the peroxide of iron test only, a solution of meconic and acetic acids might possibly be confounded with that of a sulphocyanide, as they also strike a red colour with a solution of a salt of the peroxide of iron. By adding to the red liquid some *solution of corrosive sublimate*, a sulphocyanide may be readily distinguished from an acetate or meconic acid; with the former the colour entirely disappears on the addition of corrosive sublimate, but the colour of the latter remains.

Soluble sulphocyanides produce a black precipitate in a tolerably strong solution of *sulphate of copper*; and in a solution of the *red oxide of copper* (or of the black oxide of copper to which some protochloride of tin is added), a white precipitate of subsulphocyanide of copper. The latter precipitate is formed in dilute solutions.

10. HYDROSULPHURIC ACID AND SULPHURETS. — The smallest traces of hydrosulphuric acid, also called sulphuretted hydrogen, can be detected by the peculiarly disagreeable odour of this gas, resembling that of putrid eggs. A jet of sulphuretted hydrogen gas takes fire in the air, on the approach of a lighted taper, producing a blue flame, and developing the odour of sulphurous acid. A mixture of sulphuretted hydrogen gas and air, or oxygen gas, detonates when inflamed.

When free sulphuretted hydrogen, or a solution of an alkaline or earthy sulphuret, is brought into contact with a solution of any *salt of lead, copper, or silver*, a black or brownish-black precipitate of metallic sulphuret appears. To detect sulphuretted hydrogen in the gaseous state, a strip of paper may be moistened with a solution of acetate, or, what is still more delicate, of subacetate of lead, and then held in the gas to be examined: if sulphuretted hydrogen is present, the paper becomes brown. Such papers may be dried and preserved in store for use, and applied dry; but some other

soluble compounds of lead and copper are not attacked by sulphuretted hydrogen, in the absence of moisture.

The sulphurets of the bases forming Class I. (page 41.) are soluble in water. These bodies are recognised by their solutions disengaging sulphuretted hydrogen gas when mixed with hydrochloric acid. When the sulphuret contains an excess of sulphur, a milky precipitate of sulphur is also produced on the addition of hydrochloric acid. The precipitate may be recognised as sulphur by its combustibility, and by developing the odour of sulphurous acid while burning.

The sulphurets of such bases of Classes II. and III. (pages 41, 42.) as form sulphurets are insoluble in water. Some are soluble, with decomposition, in hydrochloric acid, and may be recognised by the odour of sulphuretted hydrogen then disengaged. Others are insoluble in hydrochloric acid, but are dissolved by hot nitric acid, the sulphur of the sulphuret being thereby converted into sulphuric acid. A few are unacted on by boiling nitric acid, but all such sulphurets are decomposed by aqua regia, with conversion of the sulphur into sulphuric acid. The metallic bases of sulphurets are commonly oxidized by nitric acid and aqua regia before the sulphur, the latter being set at liberty and dissolved slowly.

11. **HYPOSULPHURIC ACID.**—Free hyposulphuric acid is a very unstable compound; when its solution in water is rapidly evaporated, the acid is resolved into sulphurous acid, which is disengaged as a gas, and sulphuric acid, which remains in the liquid. Compounds of this acid with bases (hyposulphates) undergo an analogous decomposition when heated in the dry state, sulphurous acid being evolved, while a neutral sulphate remains. In applying this character as a test for a hyposulphate, the substance may be heated by a spirit lamp, in a glass tube sealed at one end. The evolved sulphurous acid is recognised by its odour, and the residuary sulphate by a salt of barytes, in the ordinary manner.

Hyposulphates are also distinguished from many other classes of salts by their general solubility, and by their comportment with hydrochloric and sulphuric acids. *Hydrochloric acid* produces no change in a solution of a hyposulphate in the

cold ; but if the mixture is heated, the hyposulphate is decomposed, sulphurous acid is disengaged, and the liquid contains a sulphate, as may be ascertained by chloride of barium. In this reaction, no deposit of sulphur or any other precipitate takes place, unless a base is present which is precipitated by sulphuric acid, as barytes, oxide of lead, &c. Hyposulphates comport with *sulphuric acid* in a similar manner ; but in this case the sulphuric acid formed through the decomposition of the hyposulphate cannot of course be detected. Hyposulphates in solution are not acted on by *nitric acid* in the cold ; but when the mixture is heated, nitrous vapours are evolved, and the *hyposulphates* are converted into *sulphates*.

The characters ascribed to the salts of *sulpho-hyposulphuric acid* (the *trithionic acid* of Berzelius, $S_3 O_5$) are the following : — the sulpho-hyposulphates of lime, barytes, strontian, magnesia, alumina, oxide of lead, oxide of iron, oxide of zinc, oxide of nickel, oxide of cobalt, peroxide of uranium, &c., are soluble in water ; therefore the application of a sulpho-hyposulphate to a solution of any one of these bases causes no precipitate. From a solution of the nitrate of suboxide of mercury, a sulpho-hyposulphate precipitates sulphuret of mercury ; and from a solution of corrosive sublimate, a precipitate of sulphate of suboxide of mercury. In a solution of nitrate of silver, a sulpho-hyposulphate forms a yellow precipitate, which soon becomes black. Free sulpho-hyposulphuric acid, in solution in water, is subject to slow spontaneous decomposition, with production of sulphurous acid, sulphuric acid, and free sulphur. (M. Langlois.)

The sulpho-hyposulphite of potash, or trithionate of potash, when exposed to heat, disengages sulphurous acid and sulphur, and leaves a residue of neutral sulphate of potash. The aqueous solution of this salt is decomposed by sulphuric acid, with disengagement of sulphurous acid and deposition of sulphur ; but hydrochloric acid does not decompose it. (M. Plessy.) Iodine is without action on the sulpho-hyposulphates, by which character that class of salts may be distinguished from the hyposulphites. From hyposulphates,

they are distinguished by affording a precipitate of sulphur when decomposed by sulphuric acid, which hyposulphates do not.

The other sulphur acid of recent discovery, the *bisulpho-hyposulphuric acid* (called by Berzelius *tetrathionic acid*, $S_4 O_5$), is said to possess the following characters. A solution of the free acid in water is colourless and inodorous, and possessed of a strong acid taste; if weak, it is not decomposed by ebullition, but at a certain degree of concentration it is resolved into sulphur, sulphuric acid, and sulphurous acid; it is not altered by sulphuric and hydrochloric acids, but nitric acid decomposes it, with separation of sulphur. This acid forms soluble salts with most bases, as the oxide of zinc, peroxide of iron, oxide of copper, oxide of lead, &c.; it produces white precipitates in solutions of protochloride of tin and corrosive sublimate, and black precipitates in solutions of nitrate of suboxide of mercury and nitrate of silver. (MM. Fordos and Gelis.)

12. **HYPOSULPHUROUS ACID.**—The compounds of hyposulphurous acid with bases (hyposulphites) resemble, in many respects, the analogous compounds of the two preceding acids, sulpho-hyposulphuric, and bisulpho-hyposulphuric. Free hyposulphurous acid spontaneously decomposes into sulphurous acid and sulphur; hence the addition of *sulphuric* or *hydrochloric acid* to a solution of a hyposulphite determines the evolution of sulphurous acid, which is recognised by its odour, and a milky precipitate of sulphur. This decomposition takes place slowly in the cold, but more rapidly at the boiling point. When a solution of a pure hyposulphite is mixed with hydrochloric acid, and heated, no sulphuric acid is found in the liquid; but if the mixture is exposed to the air for some time, it may be found to contain a trace of sulphuric acid, through the absorption of oxygen by the sulphurous acid.

The white precipitate produced by *nitrate of silver* in a solution of a hyposulphite (see the Table, page 137.) is hyposulphite of silver. This precipitate soon becomes yellow, and

at length black, in which state it consists of sulphuret of silver.

A solution of a hyposulphite possesses the remarkable property of dissolving a considerable quantity of recently precipitated chloride of silver, forming a solution which has an extremely sweet taste. This solution does not afford a deposit of sulphuret of silver by ebullition or long standing.

A strong solution of *chloride of barium* produces a white precipitate of hyposulphite of barytes in a strong solution of a hyposulphite; but no precipitate is formed unless both solutions are concentrated.

13. NITRIC ACID. — Nitric acid forms soluble salts with all the metallic oxides with which it combines: a few oxides, however, among which are the protoxide of copper (black oxide) and oxide of bismuth, form insoluble subnitrates, as well as soluble nitrates, containing a larger proportion of nitric acid. When exposed to a red heat, nitrates of the alkaline bases are decomposed, with disengagement of a mixture of oxygen and nitrogen gases; other nitrates disengage oxygen, and red fumes of nitrous acid, on being strongly heated. As the tests for free nitric acid and nitrates are not so delicate as those for most other acids, it is advisable, when the subject of examination is a dilute solution, to concentrate it by evaporation. If the liquid contains a free acid, this must be carefully neutralized by potash before evaporation. The dry residue may then be examined for nitric acid by the following tests. .

If mixed with *copper* or *brass filings*, and this mixture drenched with *sulphuric acid* slightly diluted (equal measures of strong oil of vitriol and water), nitrates disengage nitric oxide gas, which immediately on coming in contact with the air gives rise to reddish-brown vapours of nitrous acid. A flask or test-tube is a convenient vessel to make use of in this experiment. The absence of nitric acid in the sulphuric acid employed for this purpose should be ensured previous to testing (see page 18.), as the oil of vitriol of commerce often contains a small quantity of nitric acid.

When a nitrate is placed in contact with a piece of *burning*

charcoal or other carbonaceous substance, a deflagration takes place, that is, the combustion of the charcoal is greatly enlivened around the nitrate, and bright sparks may be projected.

A mixture of a nitrate with *hydrochloric acid* possesses the property of dissolving gold when heated; but hydrochloric acid alone does not. Leaf gold should be used in applying this character as a test for a nitrate.

Free nitric acid, and therefore a mixture of a nitrate with sulphuric acid, is capable of bleaching a solution of sulphate of indigo with the aid of heat. This test is delicate, but not very certain, as free chlorine and some other substances also decolorize sulphate of indigo. The following test is worthy of more confidence.

When a solution of a nitrate is mixed with from one-fifth to one-third its volume of strong sulphuric acid, and a few crystals of protosulphate of iron (copperas) added to the mixture, the liquid surrounding the crystals acquires a deep brown colour. The nitric acid of the nitrate, liberated by the sulphuric acid, is resolved into nitric oxide and oxygen; the latter combines with a part of the protoxide of iron to form the peroxide of iron, while the nitric oxide combines with another portion of protoxide of iron to form the brownish-black compound which is the source of colour. If the copperas is applied in too small a quantity, the colour may entirely disappear on agitation, the whole of the protoxide of iron being converted into peroxide of iron, which does not, like the protoxide, form a brown compound with nitric oxide. If the solution of the nitrate is dilute, no production of colour may take place till the mixture is heated; but the continued application of heat discharges the brown colour. Iodides and bromides also give rise to the production of a purplish or brownish colour with the above test; but this disappears on the application of a large excess of protosulphate of iron, while the colour produced by nitric acid does not. (Schweitzer.)

The following test for nitric acid, recommended by M. Berthémot, is said to detect the presence of that acid, when mixed with 10,000 times its volume of other liquid. About

half a drachm, by measure, of concentrated sulphuric acid, free from nitric acid, is poured into a test-glass, and mixed with a little (a few drops merely) of the liquid under examination. A particle of *brucine* is then added to the mixture, and the whole well stirred. If nitric acid is present, the liquid presently becomes red, and afterwards yellow; but if no nitric acid exists in the mixture, the brucine does not dissolve.

Nitrates may be distinguished from the salts of nearly all other inorganic acids, by affording no precipitate either with chloride of barium or nitrate of silver. Chlorates, however, resemble nitrates in this respect, and also in the property of deflagrating with burning charcoal, in that of bleaching sulphate of indigo in the presence of free sulphuric acid, and in that of dissolving gold in the presence of hydrochloric acid. Nitrates may, however, be distinguished from chlorates with certainty by the test of sulphuric acid and copper filings, and by that of sulphuric acid and copperas. To discover a chlorate in the presence of a nitrate, the substance should be heated to redness, whereby the chlorate becomes converted to a chloride, which may be detected in the solution of the calcined mass by nitrate of silver, some free nitric acid being also added.

14. NITROUS ACID.—Free nitrous acid, in the gaseous state, is recognised by its peculiar reddish-brown colour. This acid undergoes a partial decomposition by contact with water.

Compounds of nitrous acid with bases, that is, nitrites, are distinguished from other classes of salts by the following characters:—1. Solutions of nitrites of the alkalies and of the alkaline earths affect test-papers as a free alkali. 2. Nitrites are decomposed by sulphuric and most other acids (even acetic), with liberation of nitrous acid, which is immediately resolved into nitric acid and nitric oxide: the latter is a colourless gas, which becomes reddish brown by contact with air or oxygen gas, owing to the formation of nitrous acid or peroxide of nitrogen. 3. When a solution of a nitrite is boiled gently in a retort, nitric oxide gas is disengaged, and a nitrate remains in the retort.

Nitrites do not, like nitrates, possess the property of dissolving gold-leaf when mixed and heated with hydrochloric acid. (p. 155.)

15. PERCHLORIC ACID. — Free perchloric acid is very soluble in water, fusible at a very moderate heat, and volatile at a high temperature. In a highly concentrated state, it is decomposed by *strong sulphuric acid* with the aid of heat, chlorine and oxygen gas being disengaged. But free perchloric acid is not decomposed by *hydrochloric acid*, *sulphurous acid*, *sulphuretted hydrogen*, or *alcohol*; by which characters it may be distinguished from free chloric acid.

All perchlorates dissolve freely in water, except the perchlorates of potash and ammonia; therefore metallic solutions afford no precipitate with solutions containing a perchlorate. The perchlorate of potash is scarcely at all soluble in water, and is insoluble in alcohol; hence a salt of potash may be used as a precipitant for perchloric acid, as well as perchloric acid for potash. (p. 49.)

Perchlorates deflagrate with combustibles in the same manner as nitrates and chlorates; and the perchlorates of the alkalis and alkaline earths, like the corresponding chlorates, are converted into chlorides by exposure to a red heat, with disengagement of oxygen gas.

Perchlorates are distinguished from chlorates (the only salts with which they are easily confounded) by not being decomposed, in the cold, by *hydrochloric acid* or *sulphuric acid*. Chlorates, when in concentrated solution, acquire a yellow colour and evolve a yellow gas on being mixed with either of these acids.

PART III.

SYSTEMATIC QUALITATIVE ANALYSIS.

PART III.

SYSTEMATIC QUALITATIVE ANALYSIS.

PRELIMINARY OPERATIONS.

THE performance of a satisfactory qualitative analysis of a complex substance by the aid of the description of the chemical characters of bodies contained in the preceding chapters, would be a matter of some difficulty in its present arrangement. But the same information, presented in a different form, will now be applied as the basis of a systematic course of qualitative analysis, simple, and easy of execution. Instead of applying each reagent successively, the method adopted in examining the composition of single or mixed bodies consists in determining the presence or absence of certain *classes* of substances by the application of a single test for each class; these classes can be divided and subdivided by other tests, and the subdivisions examined for their individual members. A particular class of metals is, for instance, precipitated by sulphuretted hydrogen; by the behaviour of this class with hydrosulphate of ammonia, it admits of a farther division, some of the metals precipitated by sulphuretted hydrogen being soluble, the remainder insoluble, in that liquid; thus affording two divisions, each of which, if both are found to exist, is then examined for its individual members.

The advantage of this method of procedure arises from its being, in general, as easy to discover a class as a particular body; and the absence of a class being demonstrated, it is of course unnecessary to examine by other tests for any particular member. The principal feature in this system is, therefore, that of exclusion; on the application of a test, hydrosulphate of ammonia, for example, when we perceive

none of the appearances which that test should produce with certain metals, we reject these as absent from the combination. We thus have a negative result; but to prove the absence of particular substances is in itself just as important in qualitative analysis as to demonstrate their presence.

A substance may occasionally be presented for examination, whose composition can be very well ascertained by the application of two or three reagents, but it is advisable, and will mostly, in the end, be found more satisfactory, especially when we are not assured of the purity of the substance under examination, to follow some general rule, or particular system, rather than to try the effect of a reagent at random, from some vague idea we had before entertained of the composition of the substance. Such systems are developed in the following tables, where, it will be seen, classes are formed, divided, subdivided, and, if necessary, divided further, characters being described by which the particular members of each subdivision are distinguished from one another.

Preliminary examination of non-metallic solids.—An examination of the physical characters of a substance must always precede its analysis. It is of importance to know its density, volatility, combustibility, and solubility. The action of heat on the substance should be particularly investigated. With this view, the body may be submitted in the first place to a complete course of blowpipe experiments, as described in the latter part of the chapter on blowpipe analysis, but more especially to the first operation, (heating in a glass tube closed at one end,) and to the operation of being heated on charcoal in the reducing flame.

Whether the substance is submitted to a complete course of blowpipe experiments or not, it is always necessary to ascertain if any *organic matter* is present, before proceeding to determine the inorganic constituents, since organic matters materially affect the behaviour of many metals with reagents, as is stated in the preceding chapters. Almost all fixed organic bodies possess the property of becoming blackened or carbonized by being heated out of contact with the air. To

discover organic matter, therefore, a small portion of the substance should be heated in a glass tube, free from lead, when, in general, blackening will occur, and an empyreumatic odour be developed, if organic matter is present. The tube should be held slightly inclined, and be heated by a spirit lamp.

There are, however, a few inorganic bodies which become black on being heated : and, on the contrary, some organic bodies which do not blacken. But there is another character of organic bodies, which differs with the blackening by heat, may be considered decisive. This is the property they all possess of deflagrating when thrown into fused nitre ; a property possessed, too, by a few inorganic bodies, but by none which also blacken on being heated. The two tests conjoined are therefore conclusive.

By the same operation of heating in a tube to discover organic matter, we ascertain whether the substance contains *water*. If so, this condenses on the sides of the glass tube before the heat is sufficient to carbonize the substance. If the condensed water is alkaline, this shows the presence of *ammonia*.

If organic matter is present, and the object of the analysis is merely to discover the fixed bases, and not the acids of the substance, it should be destroyed by combustion in the open air, either in a platinum or a porcelain * crucible, uncovered, heated very strongly by a spirit lamp with circular wick, or by the inflammable mixture of gas and air described page 10.

After having ascertained the action of heat on the substance under examination, that of *solvents* must next be determined. Water, hydrochloric acid, nitric acid and aqua regia, are the liquids generally used as solvents in chemical analysis. According to their solubility in certain liquids, all substances admit of classification, which is taken advantage of in qualitative analysis ; it is to be borne in mind, however, that in

* When the substance can contain metals reducible by charcoal, and which would alloy with platinum at a red heat, a porcelain crucible must be used ; in other cases platinum is preferable.

many cases, such classification is not exact, or rather not of easy application, owing to the very slight degree of solubility of some substances in certain liquids, which would induce beginners to pronounce such substances insoluble in the liquids in question. This is the case with sulphate of lime and water for example.

The first liquid whose solvent power on the substance is to be examined is pure distilled water. For this purpose a portion of the substance, in fine powder, is mixed with eight or ten times its bulk of water in a flask or basin, to which, if complete solution does not soon take place, heat may be applied, in order to bring the water to the boiling point. If the substance completely dissolves in water, the solution is examined according to the course prescribed in Section I. of the following Chapter (page 168.), or in Section I. of Chap. II. (page 184.)

If the substance is not entirely, but partially, soluble in water, the aqueous solution is separated by filtration from the undissolved residue, which is subjected to the action of acid solvents, and the solution is further examined as if the substance had been wholly soluble. To ascertain whether the water has dissolved any portion of the substance, a drop of the filtered water is evaporated upon a piece of clean platinum foil: if no residue appears, the substance is entirely insoluble in water. The original substance, if entirely insoluble in water, or the portion undissolved by water, if it is partially soluble, is then digested, first in hydrochloric acid, secondly in nitric acid, or, thirdly, in aqua regia, until it dissolves entirely, or leaves only a slight residue, which must be collected and examined in other ways. The solvent power of hydrochloric acid, cold and hot, should always be tried first. The greater number of substances which are insoluble in water but soluble in acids, do not dissolve in acids without decomposition, and with many classes of bodies, during such decomposition, certain appearances are presented which afford an indication of the nature of the substance under examination. Thus effervescence of an inodorous gas indicates the presence of carbonates; when hydrochloric acid

is the solvent, the disengagement of sulphuretted hydrogen evidences the presence of a certain class of sulphurets; the disengagement of hydrocyanic acid, that of cyanides; the disengagement of chlorine, that of peroxides, &c. Acids frequently leave insoluble residues, which have been formed by their action on the substance to be dissolved, and did not therefore pre-exist in the substance under examination in the form in which they are separated: these may be easily distinguished in appearance from the original substance; thus silica remains as a jelly when some silicates are treated with acids; sulphur when sulphurets, and selenium when seleniurets are acted on by nitric acid. In the last two cases, sulphur and selenium are slowly dissolved by the further action of the acid, sulphuric and selenic acids being formed. The acid solution of the substance, whether hydrochloric acid, nitric acid, or aqua regia is employed, is then examined according to the course prescribed in Section II., Chap. II.

The course of qualitative analysis of the substances insoluble in water and in hydrochloric acid, nitric acid, and aqua regia is described in Section III., Chapter I. (page 181.), where a single acid and a single base is supposed to be the subject of experiment; and that of a mixture of such bodies in Section III. Chap. II. The substances which are insoluble in acids (as is the case with most silicates) may generally be rendered soluble by fusion with an alkaline carbonate. This operation consists, 1. in reducing the substance to a state of extremely minute division in an agate mortar; 2. mixing with twice or thrice its weight of pure carbonate of soda or potash; and 3. fusing the mixture in a covered platinum crucible. The resulting mass is then treated with pure hydrochloric or nitric acid, and is in almost every case dissolved, leaving, in the case of silicates, a gelatinous residue of silicic acid. (See the Analysis of Silicates for details of this operation.) When fusion with carbonate of soda is inadequate, caustic potash (*potassa fusa*) is to be substituted, and the fusion performed with care in a silver instead of a platinum crucible.

Metals and metallic alloys. — Nitric acid is the most important solvent for a metal or a metallic alloy. Most metals are completely dissolved by this acid, being converted into nitrates; antimony and tin are oxidized by this acid without solution, and platinum, gold, and a few other metals are not altered by it. If the metal is converted by hot nitric acid into a white powder, which does not dissolve on the addition of water, this powder is examined before the blowpipe for antimony and tin; if the metal or a portion of it remains unacted on, this residue is digested in aqua regia, which very rarely fails to produce complete solution. The solution, whether obtained by nitric acid or aqua regia, is examined according to the course prescribed in Section II. Chap. I., or Section II. Chap. II.

Liquids. — If the liquid contains any solid body in solution (which is ascertained by evaporating a drop to dryness on a piece of clean platinum foil) and does not affect test-paper in the manner of an acid, it is examined according to the mode prescribed for substances soluble in water. But if the liquid has an acid reaction, it may be examined as containing a substance insoluble in water but soluble in acids. It is to be observed, however, that the acid reaction may not proceed from a free acid, but from a metallic salt of neutral constitution, in which case the liquid may be examined as containing a substance soluble in water. If the acid reaction proceeds entirely from a metallic salt of neutral constitution, a portion of the liquid becomes turbid when mixed with a very minute quantity of an alkaline liquid, which turbidity generally remains after agitation. But if a free acid is present, the turbidity disappears on agitation. If alcohol, ether, or other organic liquid appears to be present, it should be got rid of by evaporation to dryness, and the dry residue be then digested in water, or, if necessary, in an acid.

The following chapter contains directions for the qualitative analysis of a salt consisting only of a single acid and a single base, comprising all those which are of ordinary occur-

rence: with such, rather than with complex substances, the beginner will do well to exercise himself.

Respecting the quantity of matter to be operated on, it will be found more convenient to work with small than with large amounts; from ten to twenty grains will be sufficient in almost every case. A small quantity must always be reserved, in case of accidents, or to examine the action of any special test.

LIST OF BASES TO BE SOUGHT FOR.

| | | | | | |
|----------|---|-----------------------|------------|---|-------------------------|
| Class I. | { | Antimony, oxide of | Class II. | { | Alumina |
| | { | Bismuth, oxide of | | { | Chromium, oxide of |
| | { | Cadmium, oxide of | | { | Cobalt, oxide of |
| | { | Copper, protoxide of | | { | Iron, protoxide of |
| | { | Gold, oxide of | | { | Manganese, protoxide of |
| | { | Iron, peroxide of | | { | Nickel, oxide of |
| | { | Lead, oxide of | | { | Zinc, oxide of. |
| | { | Mercury, protoxide of | Class III. | { | Barytes |
| | { | Mercury, suboxide of | | { | Lime |
| | { | Silver, oxide of | | { | Magnesia |
| | { | Tin, peroxide of | | { | Strontian |
| | { | Tin, protoxide of. | | { | Ammonia |
| | | | | { | Lithia |
| | | | | { | Potash |
| | | | | { | Soda. |

LIST OF ACIDS TO BE SOUGHT.

| | |
|----------------------------|-----------------------------|
| Arsenic and arsenious | Hydrosulphuric (or sulphur) |
| Boracic | Iodic |
| Carbonic | Nitric |
| Chloric | Phosphoric |
| Hydrochloric (or chlorine) | Silicic |
| Hydrofluoric (or fluorine) | Sulphuric |
| Hydriodic (or iodine) | Sulphurous. |

CHAPTER I.

QUALITATIVE ANALYSIS OF A SALT SUPPOSED TO CONSIST OF A SINGLE ACID AND A SINGLE BASE, CONTAINED IN THE PRECEDING LIST.

SECTION I.

QUALITATIVE ANALYSIS OF A SALT SOLUBLE IN WATER, SUPPOSED TO CONTAIN ONE ACID AND ONE BASE.

(A). Detection of the Base.

THE first operations in the qualitative examination of a substance for its base have for their object the assignment of the base to one of the three classes in the preceding list. Class I. is precipitated by sulphuretted hydrogen from a solution containing a free acid; Class II. is not precipitated by sulphuretted hydrogen from an acid solution, but it is by hydrosulphate of ammonia from a neutral solution; Class III. is not precipitated either by sulphuretted hydrogen or hydrosulphate of ammonia. In acidifying the solution by hydrochloric acid, previous to the application of sulphuretted hydrogen, the presence or absence of oxide of silver, suboxide of mercury, and, if the solution is tolerably strong, of protoxide of lead, is determined. The course of operation is the following.

1. Render a portion of the aqueous solution of the substance perceptibly acid by the addition of a little hydrochloric acid.

The production of a white precipitate by hydrochloric acid indicates the presence of either oxide of silver, suboxide of mercury, or

protoxide of lead. To one portion of the mixture of the precipitate with the liquid, add an excess of ammonia : if the precipitate is redissolved, the base is *silver*, (page 97.) ; if the precipitate is blackened by ammonia, but not dissolved, the base is *suboxide of mercury*, (page 92.) ; if the precipitate is unaltered by ammonia, the base is *protoxide of lead* (page 91.), in which case the precipitate produced by hydrochloric acid completely dissolves when warmed with a considerable quantity of water. If the solution of the substance under examination is dilute, lead may be present, and yet no precipitate be produced by hydrochloric acid.

2. If no precipitate is produced by the application of hydrochloric acid, pass sulphuretted hydrogen gas through the acidified liquid, or add sulphuretted hydrogen water to it.

If a precipitate is produced in the acidified liquid by sulphuretted hydrogen, it consists of the sulphuret of one of the following metals :

| | |
|---------|--------------------------|
| Cadmium | Mercury (two sulphurets) |
| Lead | Gold |
| Bismuth | Tin (two sulphurets) |
| Copper | Antimony |
| Silver | |

together with sulphur, caused by a persalt of iron, and sulphuret of arsenic from arsenious or arsenic acid.

a. If the colour of the precipitated sulphuret is *black*, or *brownish black*, the base may be one of the following :

1. *Protoxide of lead*. — To discover the presence of lead, apply to the original solution the tests of sulphuric acid and chromate of potash (page 91.).

2. *Oxide of bismuth*. — If bismuth is present, the saturated solution of the substance becomes milky on dilution with water, and the milkiness is not removed by the application of tartaric acid (pages 85, 86.). It is scarcely possible, however, for bismuth to be present in a solution containing no free acid.

3. *Protoxide of copper*. — To discover the presence of protoxide of copper, apply to the original solution the tests of ammonia (in excess) and yellow prussiate of potash (pages 78, 88.).

4. *Oxide of gold*. — Apply to the original solution protochloride of tin, mixed with a little perchloride of tin (page 89.)

5. *Protoxide of tin*. — To discover this oxide, add perchloride of gold to the original solution (page 98.).

6. *Protoxide of mercury*. — Apply the tests, caustic potash (page 80.), and iodide of potassium (pages 93, 94.) to the original solution ; and try the blowpipe test for mercury on the dry substance.

7. *Suboxide of mercury*, and

8. *Oxide of silver*, also afford black precipitates of sulphurets with sulphuretted hydrogen, but the presence or absence of these oxides has already been determined by the application of hydrochloric acid, at the commencement of the examination.

b. If the colour of the precipitated sulphuret is orange-red, the base may be :

9. *Oxide of antimony.* — Filter and dry the precipitated sulphuret, and then dissolve it in hot hydrochloric acid ; evaporate off most of the excess of acid, and pour the remaining solution into water ; if the base is antimony, a white precipitate of basic chloride is formed (page 85.).

c. If the colour of the precipitate produced by sulphuretted hydrogen is *yellow or milk-white*, the base may be oxide of cadmium, peroxide of tin or peroxide of iron ; or one of the acids of arsenic may be present.

10. *Oxide of cadmium.* — This oxide is recognised by its neutral solution affording, with hydrosulphate of ammonia, a yellow precipitate *insoluble* in excess of hydrosulphate of ammonia.

11. *Peroxide of tin.* — If the base is peroxide of tin, the yellow precipitate produced by sulphuretted hydrogen is soluble in hydrosulphate of ammonia, and does not volatilize when heated before the blow-pipe.

Arsenious and arsenic acids. — These acids are detected in the course of the examination for the base. The yellow precipitates which their solutions afford with sulphuretted hydrogen are soluble in hydrosulphate of ammonia, and volatilize at a high temperature. The presence of arsenic in the precipitate should be confirmed by the blowpipe test ; and in the original solution by sulphate of copper (pp. 105. 107.), and also by nitrate of silver (p. 100.), which affords the means of distinguishing between arsenious acid and arsenic acid.

12. *Peroxide of iron.* — The precipitate produced by sulphuretted hydrogen when peroxide of iron is the base is nothing more than *sulphur*, the cause of formation of which, in such circumstances, is explained in the note, page 41. If peroxide of iron is the base, the yellow prussiate of potash produces in the original solution a precipitate of prussian blue (page 67.), and the red prussiate produces a similar precipitate in the solution which has been exposed to sulphuretted hydrogen, but not in the original solution (page 68.).

3. If sulphuretted hydrogen causes no precipitate in the acidified solution of the substance, add to the same liquid, first ammonia, until the hydrochloric acid present is neutralized, and then some hydrosulphate of ammonia ; or else, add to the original solution first, muriate of ammonia, and then, hydrosulphate of ammonia.

If no precipitate is produced by sulphuretted hydrogen in the acidified solution, but one is produced by hydrosulphate of ammonia in a neutral or alkaline liquid containing muriate of ammonia, the base is then one of Class II. (page 167.)

a. If the colour of the precipitate produced by hydrosulphate of ammonia is *black*, the base is either oxide of nickel, oxide of cobalt, or protoxide of iron.

1. *Oxide of nickel*. — The original solution gives an apple-green precipitate with a solution of carbonate of potash, and a similar precipitate with caustic potash. With ammonia, it gives a green precipitate, soluble in excess of ammonia, and re-precipitated from the ammoniacal solution by potash.

2. *Oxide of cobalt*. — Carbonate of soda produces in the original solution, a dull red precipitate, which becomes blue by boiling the liquid. As a confirmatory test, potash may be applied to the original solution (see the comportment of potash with solution of cobalt, page 56.); and a small fragment of the solid under examination may be fused with borax before the blowpipe. (See the chapter on Blowpipe Analysis.)

3. *Protoxide of iron*. — Carbonate of soda produces a greenish precipitate, which becomes reddish on exposure to the air. Apply the red prussiate of potash to the original solution (page 68.).

b. If the precipitate produced by hydrosulphate of ammonia has a *dull green* colour, the base is :

4. *Oxide of chromium*. — The presence of oxide of chromium is then confirmed by applying potash to the original solution (see page 56.). The substance should also be examined before the blowpipe. (See the chapter on Blowpipe Analysis.)

c. If the precipitate produced by hydrosulphate of ammonia has a *flesh-colour*, the base is :

5. *Protoxide of manganese*. — Potash is applied to the solution of the substance as a confirmatory test (see page 58.), and the substance itself should be examined before the blowpipe with microcosmic salt. (See the chapter on Blowpipe Analysis.)

d. If the precipitate produced by hydrosulphate of ammonia is *white*, the base is either alumina or oxide of zinc.

6. *Alumina*. — If the base is alumina, the original solution affords with ammonia a white gelatinous precipitate, insoluble in excess of ammonia, but soluble in caustic potash.

7. *Oxide of zinc*. — If the base is oxide of zinc, the original solution gives a white precipitate with ammonia, soluble in excess of ammonia, as well as in caustic potash. The solution of oxide of zinc in caustic potash affords a white precipitate with sulphuretted hydrogen, which is not the case with the potash solutions of alumina and oxide of chromium.

4. If neither sulphuretted hydrogen nor hydrosulphate of ammonia produces a precipitate, the base is one of Class III. (page 167.) To a portion of the original solution, *rather dilute*, add a solution of carbonate of soda.

If a precipitate is produced by carbonate of soda, and none by hydrosulphate of ammonia, the base is either barytes, lime, strontian,

or magnesia. If the solution of the substance is very strong, and not somewhat diluted as above directed, a precipitate of carbonate of lithia may be gradually produced. This does not occur, however, in a moderately dilute liquid.

1. To a portion of the original solution in a concentrated state add sulphuric acid. If no precipitate appears the base is *magnesia*. This result is confirmed by applying to a portion of the original solution the test of phosphate of soda with ammonia (page 54.).

2. To another portion of the original solution, add a solution of sulphate of lime: if a precipitate appears *immediately*, the base is *barytes*.

3. If solution of sulphate of lime produces in the concentrated original solution a precipitate after the lapse of a quarter of a hour, but none at first, the base is *strontian*. This indication of the presence of strontian is confirmed by exposing the substance to the alcohol flame (page 53.).

4. If solution of sulphate of lime produces no precipitate after the lapse of a quarter of an hour, but a strong solution of sulphate of soda does in the concentrated original solution, the base is *lime*. This result is confirmed by adding oxalate of ammonia to the original solution in a diluted state.

5. If carbonate of soda produces no precipitate in the slightly diluted solution, the base is either potash, soda, ammonia, or lithia.

1. *Ammonia*. — The test of potash is first applied to the original solution (page 51.).

2. *Potash*. — After the absence of ammonia has been proved, test the original solution for potash with tartaric acid and chloride of platinum (page 48.).

3. *Lithia*. — To detect the presence of lithia, apply to the concentrated solution of the substance the tests, carbonate of soda and phosphate of soda with ammonia; and observe the action of the dry substance on flame (page 50.).

4. *Soda*. — The original solution is tested with antimoniate of potash (page 49.), and the dry substance is exposed to the blowpipe flame or alcohol flame (page 50.).

(B). *Detection of the Acid contained in a single salt, soluble in water, the acid being one mentioned in the list, page 167.*

After having determined the nature of the base, that of the acid may generally be ascertained by a very small number of experiments, as the most part of bases form combinations soluble in water with comparatively a small number of acids. Potash, soda, lithia, and ammonia, are the only bases which form compounds soluble in water with all the acids mentioned at page 167. The only acids, therefore, which need be sought

are those which form salts soluble in water with the base which has been already detected.

1. Mix a portion of the solid under examination with some dilute sulphuric acid (made by mixing one measure of oil of vitriol with two or three measures of water). If effervescence occurs, the acid is either carbonic, sulphurous, or hydrosulphuric. If the mixture has a brown tinge, hydriodic acid may be present.

1. *Carbonic acid*. — The gas evolved on the application of sulphuric acid is inodorous, and when passed through lime-water produces a white precipitate of carbonate of lime, which dissolves when an excess of gas is passed through the liquid (see page 122.).

2. *Sulphurous acid*. — The gas disengaged by sulphuric acid has the pungent smell of burning sulphur. This indication of the presence of sulphurous acid is confirmed by the application of iodic acid and starch (see page 133.).

3. *Hydrosulphuric acid or sulphuretted hydrogen*. — The evolved gas has a strong foetid odour, and blackens a piece of paper impregnated with a salt of lead (page 150.).

If the mixture of the solid under examination with dilute sulphuric acid has a brown tinge, which gradually deepens on exposure to the air, the acid may be :

4. *Hydriodic acid*, or iodine in combination with one of the metallic bases of the oxides mentioned at page 167. This indication is confirmed by applying starch to the mixture of the substance with nitric acid (see page 148.).

2. If sulphuric acid produces neither effervescence nor a brown tinge owing to the liberation of iodine, add a solution of chloride of barium to a portion of the solution of the substance under examination in a *neutral* and concentrated state. If the solution of the substance has an acid reaction, it may be neutralized by ammonia; if an alkaline, by dilute nitric acid.* The acids which may be precipitated by chloride of barium are sulphuric, silicic, phosphoric, arsenic, boracic, hydrofluoric, and iodic.

1. *Sulphuric acid*. — If the precipitate produced by chloride of barium is neither dissolved nor altered in appearance by hydrochloric acid, not even on the application of heat, the acid is sulphuric (see page 132.).

* If no other acid is afterwards detected in such a case but nitric acid, the neutralization is effected by sulphuric acid, and nitric acid then sought.

2. *Silicic acid*. — If the acid in question is silicic, the precipitate produced by chloride of barium is either completely dissolved by hydrochloric acid, or else is principally dissolved, *some white flakes only remaining undissolved*, which disappear on largely diluting a portion of the mixture with water. Evaporate the other portion of the mixture with hydrochloric acid to dryness, and treat the residue with hydrochloric acid and water. If a light white powder remains undissolved, the acid is silicic. This result should be confirmed by the blowpipe test for silicic acid (see page 131., and the chapter on Blowpipe Analysis).

3. *Phosphoric acid*. — After having proved the absence of silicic acid, to discover phosphoric acid, apply the tests, nitrate of silver and a salt of magnesia with ammonia (page 127.).

4. *Arsenic acid*. — This acid, as well as arsenious acid, has already been detected, if present, in the course of the examination for the base.

5. *Boracic acid*. — The property possessed by free boracic acid of tinging the flame of alcohol green is applied as the test for boracic acid, in the manner described at page 122., when the boracic acid is in combination with a base. Borate of barytes is not precipitated from *dilute* solutions, therefore the absence of boracic acid is not to be inferred from no precipitate being produced in the original solution by chloride of barium. Ammoniacal salts also prevent the precipitation of borate of barytes.

6. *Hydrofluoric acid*, or *fluorine in combination with one of the metallic bases of the alkalis mentioned at page 167.* — The action of free hydrofluoric acid on glass is taken advantage of as the best test for a fluoride. (See page 124. for the manner of applying this character as a test.)

7. *Iodic acid*. — To discover either free iodic acid or an iodate, apply the test of sulphurous acid and starch, described at page 125.

3. If the absence of the preceding acids has been proved, add a solution of nitrate of silver to the original solution, in a neutral state, or acidified with nitric acid. The production of a precipitate indicates the presence of either hydrochloric acid or hydriodic acid.

1. *Hydrochloric acid* or *chlorine*. — The precipitate produced by nitrate of silver is white, and dissolves with ease in ammonia (page 140.).

2. *Hydriodic acid* or *iodine*. — The precipitate produced by nitrate of silver has a yellowish tinge, and is nearly insoluble in ammonia. This acid, if present, has already been detected (page 173.).

4. If neither chloride of barium nor nitrate of silver produces any precipitate in the solution of the substance, the acid is either nitric or chloric. Both dry nitrates and dry chlorates deflagrate when placed on a piece of burning charcoal.

1. *Nitric acid*. — To detect nitric acid, apply the tests of sulphuric acid with copper filings, and sulphuric acid with protosulphate of iron (page 155.).

2. *Chloric acid*. — To detect chloric acid, add oil of vitriol to the dry salt; a yellow vapour (peroxide of chlorine) is evolved, which bleaches vegetable colouring matters.

SECTION II.

QUALITATIVE ANALYSIS OF A SUBSTANCE SUPPOSED TO CONSIST OF ONE ACID AND ONE BASE (CONTAINED IN THE LIST AT PAGE 167.), INSOLUBLE, OR BUT SLIGHTLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

(A). *Detection of the Base.*

The principal substances which belong to this class are arseniates, borates, carbonates, sulphurets, phosphates, and silicates of nearly all the bases in the list at page 167., excepting potash, soda, and ammonia. For the manner of obtaining solutions of such substances, see the remarks introductory to the present chapter (page. 164.).

1. A portion of the solution of the substance in an acid is largely diluted with water: if the solution becomes milky, oxide of antimony or oxide of bismuth may be present.

1. *Oxide of antimony*. — On adding tartaric acid to the milky liquid, the milkiness disappears, if the base is oxide of antimony.

2. *Oxide of bismuth*. — If the milkiness does not disappear by the addition of tartaric acid, but does by that of acetic acid, the base is oxide of bismuth.

As, however, the oxides of antimony and bismuth might not be precipitated by dilution with water in all cases, they are likewise to be regarded in the subsequent examination, supposing no precipitate to occur on dilution with water.

2. The diluted solution is either exposed to sulphuretted hydrogen gas, or mixed with sulphuretted hydrogen water.

If a black sulphuret appears, the base is one of the following:

1. *Protoxide of lead*

2. *Oxide of bismuth*

3. *Protoxide of copper*

4. *Oxide of gold*

5. *Protoxide of tin*

6. *Protoxide of mercury*

7. *Suboxide of mercury*, and

8. *Oxide of silver*, are not soluble in hydrochloric acid. Suboxide

} For the detection of these oxides
apply the tests mentioned in the
preceding section, page 169.

of mercury dissolves in aqua regia with conversion into the protoxide of mercury, and an excess of strong nitric acid produces the same change. If the base is either suboxide of mercury or oxide of silver, a white precipitate is produced on adding hydrochloric acid to the nitric acid solution: on applying an excess of ammonia to such a mixture, the precipitate becomes black, if the base is suboxide of mercury, and completely dissolves, if the base is oxide of silver.

If an *orange-red* precipitate is produced by sulphuretted hydrogen, the base is

9. *Oxide of antimony.* — Confirm this result by the experiment described at page 170.

If sulphuretted hydrogen produces a yellow or milk-white precipitate, the base may be oxide of cadmium, peroxide of tin, or peroxide of iron; or one of the acids of arsenic may be present. The yellow precipitate may also consist of nothing more than sulphur, produced from the sulphuretted hydrogen by the action of certain acids which may be present in the solution, among which acids are nitric, iodic, bromic, sulphurous, and chromic, and free chlorine or aqua regia.

1. *Oxide of cadmium*, and

2. *Peroxide of tin.* — Add ammonia to a portion of the original solution, *until the whole of the free acid is neutralized*, and then apply hydrosulphate of ammonia. If a yellow precipitate appears, insoluble in a large excess of hydrosulphate of ammonia, the base is oxide of cadmium. But if the yellow precipitate dissolves on the application of an excess of the hydrosulphate, and does not volatilize when heated before the blowpipe, the base is peroxide of tin.

3. *Peroxide of iron.* — (See the preceding Section, page 170.)

Arsenious and arsenic acids. — The precipitate of sulphuret of arsenic produced from arsenious or arsenic acid by sulphuretted hydrogen in an acid solution, volatilizes completely when heated before the blowpipe, is soluble in ammonia, and may be re-precipitated from the ammoniacal solution by hydrochloric acid. The existence of arsenic in the precipitated sulphuret should be confirmed by the process described at page 108.

If the precipitate produced by sulphuretted hydrogen is yellow, and very fusible and inflammable (burning with a blue flame), if it volatilizes completely, and does not dissolve in ammonia, it is merely sulphur, and the whole of the base still remains in solution.

3. If sulphuretted hydrogen produces no precipitate, or nothing more than a precipitate of sulphur, a portion of the acid solution is supersaturated with ammonia, and then mixed with hydrosulphate of ammonia.

If a *black* precipitate appears, the base is either *oxide of nickel*, *oxide of cobalt*, or *protoxide of iron*. Apply the blowpipe tests for these oxides, and also the tests mentioned at page 171.

If a *greenish* precipitate is produced by ammonia and hydrosulphate of ammonia, *oxide of chromium* may be present. Apply the blowpipe test for this oxide. Fusion with carbonate of soda and nitre is the most certain means of detecting the presence of oxide of chromium (page 65.).

If hydrosulphate of ammonia produces in the ammoniacal liquid a *flesh-colour* precipitate, or if ammonia produces a precipitate which acquires a flesh colour on the application of hydrosulphate of ammonia, the base is *protoxide of manganese*. Apply the blowpipe test for manganese.

In the case of a substance soluble in water, no other white precipitate would be produced (in this stage of the examination), by ammonia and hydrosulphate of ammonia, but alumina or sulphuret of zinc. But if the substance is insoluble in water, the precipitate might likewise contain one of the alkaline earths (magnesia, lime, strontian, or barytes,) united with phosphoric, boracic, oxalic, or arsenic acid. It might also contain silicic acid; for which reason it is advisable to apply to the acid solution of the substance the special test for silicic acid (page 131.), and if that acid is found to be present, to remove it by evaporation to dryness, re-solution in dilute acid and filtration, before proceeding to examine for the substances above mentioned.

After having thus separated the silicic acid, and ascertained that a white precipitate is produced, when, first ammonia, and then hydrosulphate of ammonia, are added to the solution, another portion of the solution is supersaturated with caustic potash. If the white precipitate at first produced completely redissolves in an excess of potash, the base is either *oxide of zinc* or *alumina*. If oxide of zinc, the potash solution affords a white precipitate of sulphuret of zinc by sulphuretted hydrogen. If alumina, the potash solution affords a white precipitate of alumina when mixed with muriate of ammonia, but no precipitate with sulphuretted hydrogen. Whether an indication is thus obtained of oxide of zinc or of alumina, the result should be confirmed by heating the substance before the blowpipe with a solution of nitrate of cobalt. (See the chapter on Blowpipe Analysis.)

If potash does not redissolve the precipitate, the latter may consist of either lime, magnesia, strontian, or barytes, in combination with phosphoric, arsenic, boracic, or oxalic acid: or it may consist of fluorine in combination with the metallic basis of one of the above earths.

To a portion of the original solution add a solution of sulphate of lime. If a white precipitate appears immediately, the base is *barytes*; if no white precipitate appears at first, but one falls after the lapse of a quarter of a hour, the base is *strontian*. The presence or absence of strontian should be confirmed by exposing the substance to the flame of alcohol (page 53.).

After the absence of barytes and strontian has been proved, add first sulphuric acid, and afterwards alcohol, to the concentrated solution of of the substance. If a white precipitate appears, the base is *lime*. If

no precipitate is formed, the base is *magnesia*. This result is confirmed by heating the substance before the blowpipe with a solution of nitrate of cobalt. (See the chapter on Blowpipe Analysis.)

Note. — More satisfactory results may sometimes be obtained, particularly when phosphoric acid is present, by applying to the solution of the substance (after having ascertained that it contains an alkaline earth in combination with one of the acids above mentioned), first, a solution of perchloride of iron, and afterwards ammonia, till an alkaline reaction appears. The mixture is then filtered, to separate the oxide or phosphate of iron from the liquid, and the latter is concentrated and examined for the alkaline earths in the manner described at page 172.

4. If neither ammonia nor hydrosulphate of ammonia produces any precipitate, mix a portion of the solution of the substance with an excess of carbonate of potash. If a precipitate appears, either immediately or after ebullition, the base is either lime, barytes, strontian, or magnesia.

Other portions of the original liquid are then neutralized, and tested for these earths in the manner described at page 172.

5. The only bases which remain to be sought are the alkalis, but the only acid in the list at page 167., which would form with an alkali a salt of difficult solubility in water, is silicic acid, and that only when present in large excess. Therefore, unless silicic acid is present in large proportion, it is useless to search for alkalis. The acid solution, however, may be evaporated to dryness, and the residue redissolved in water, and examined for the fixed alkalis by the tests mentioned at page 172.

(B). *Detection of the Acid contained in a single salt, insoluble in water, but soluble in acids, the acid being one of those mentioned in the list, page 167.*

Arsenic and arsenious acids have already been detected, if present, in the course of the examination for the base. Chloric acid is never found in substances insoluble in water.

1. If effervescence occurs when the substance is dissolved in hydrochloric acid, the acid may be carbonic or sulphurous, or the substance may be a sulphuret of one of the metals of Class II. (page 167.) In the latter case, the gas disengaged by hydrochloric acid is sulphuretted hydrogen.

See the manner of distinguishing between carbonic acid, sulphurous acid, and sulphuretted hydrogen, described at page 173.

2. If insoluble in hydrochloric acid, a portion of the powdered substance is next heated with pure nitric acid.

Sulphur. — The disengagement of ruddy fumes, and the separation of a yellow powder, which dissolves or aggregates into little lumps as the action proceeds, are indications of the presence of a sulphuret. If the clear nitric acid solution gives a white precipitate with chloride of barium, which does not disappear on the addition of a large quantity of water, the substance is a sulphuret.

3. The dry substance is mixed and heated with concentrated sulphuric acid.

1. *Iodine.* — If the substance is an iodide, vapours of iodine are then disengaged, and are recognised by their violet colour, and by their action on starch mucilage, which may be placed upon a piece of white paper and suspended over the mixture. A glass test-tube may be conveniently used in this experiment.

2. *Fluorine.* — The disengagement of a vapour which corrodes glass when the substance is heated with concentrated sulphuric acid is an evidence of the presence of fluorine. To detect fluorine, the mixture of the substance with sulphuric acid should be contained in a platinum crucible, which is covered with a glass plate, prepared as described at page 124.

3. *Boracic acid.* — To discover the presence of boracic acid, add alcohol to the mixture of the substance with sulphuric acid, after being heated: if the substance is a borate, the alcohol burns with a green flame (see page 122.).

4. Evaporate a portion of the clear acid solution to dryness, and digest the residue in hot hydrochloric acid.

Silicic acid. — If a white insoluble residue appears, the substance may be a silicate. Examine this residue by the blowpipe test for silicic acid.

5. The hydrochloric acid solution obtained in the last experiment is mixed with a few drops of a solution of chloride of barium.

Sulphuric acid. — The production of a white precipitate, which does not disappear on dilution with pure water, proves the presence of a sulphate.

6. *Phosphoric acid.* — If the base of the substance under examination is an oxide of Class I. p. 167. (already ascertained in the examination for the base), pass sulphuretted hydrogen through the original solution to saturation, filter, and to one

portion of the filtered liquid add excess of ammonia and a solution of magnesia. The formation of a white crystalline precipitate, insoluble in solution of muriate of ammonia, is an indication of the presence of phosphoric acid. Another portion of the filtered liquid is boiled to expel sulphuretted hydrogen, exactly neutralized with ammonia, and tested for phosphoric acid with nitrate of silver. (See page 127.) But if it has been ascertained that the base is one of Class II. p. 167., or one of the alkaline earths, the presence or absence of phosphoric acid is determined by the successive application of perchloride of iron, ammonia, and hydrosulphate of ammonia, then filtering, and testing the filtered liquid with a solution of magnesia. (See the description of this test for phosphoric acid at pp. 127, 128.)*

7. *Chlorine*.—The clear solution of the substance in nitric acid is mixed with a little nitrate of silver. If a white curdy precipitate is thereby formed, which dissolves completely in ammonia, and fuses without decomposition when heated in a porcelain capsule by a spirit lamp, the substance is a chloride. If the substance is insoluble in nitric acid, it should be boiled with a pure solution of potash, and the liquid, after filtration and supersaturation with nitric acid, should be tested for chlorine with nitrate of silver. (See page 141.)

8. The only acids in the list, which remain to be sought, are iodic and nitric. The presence of one of these is indicated by the appearance of deflagration when a fragment of the substance is placed on a piece of burning charcoal. If a deflagration is perceived, the substance is further examined as follows:—

1. *Nitric acid*.—The substance is heated in a tube with a mixture of equal volumes of oil of vitrol and water, and a few copper filings. If

* The detection of phosphoric acid, when combined with alumina, is rather more difficult. The comportment of phosphate of alumina with most reagents is precisely the same as that of alumina; so that the remarks in the preceding and following section, on the detection of alumina, apply also to phosphate of alumina. To detect the phosphoric acid in this compound, the process of M. Fuchs for its quantitative analysis (described under the head of Phosphorus) may be followed: or the substance may be dissolved in a small quantity of hydrochloric acid, the solution mixed with a tolerably large quantity of tartaric acid, and then supersaturated with ammonia. In the presence of tartaric acid, phosphate of alumina is not precipitated by ammonia; but if a solution of a salt of magnesia is added to that ammoniacal liquid, a precipitate of ammonio-phosphate of magnesia is produced. (M. Fresenius.)

nitric acid is present, red vapours of nitrous acid are perceived. Almost the only compounds of nitric acid insoluble in water, are subnitrate of copper, and subnitrate of bismuth. When these substances are heated, ruddy vapours of nitrous acid are disengaged.

2. *Iodic acid*.—To discover the presence of iodic acid, the substance is heated in a glass test-tube, and if violet vapours of iodine are not then disengaged, the residue is tested for iodine, by being heated with concentrated sulphuric acid, as before described. (See page 147. and also page 125.)

SECTION III.

QUALITATIVE ANALYSIS OF A SUBSTANCE SUPPOSED TO CONSIST OF ONE ACID AND ONE BASE (CONTAINED IN THE LIST, PAGE 167.), INSOLUBLE, OR BUT SLIGHTLY SOLUBLE, IN WATER AND ACIDS.

The substances to be considered under this head are the following : — sulphates of barytes, lead, lime, and strontian; chloride of silver, silica, and some silicates; some acid arseniates, after having been strongly calcined; and the insoluble modifications of peroxide of tin, peroxide of iron, and oxide of chromium. If we are acquainted with the physical characters of all these substances, a few simple experiments will suffice for the detection of the body under examination; but if not, a systematic course of experiments must be performed, much resembling that detailed in the preceding section.

1. The substance, in fine powder, is mixed with three or four times its weight of carbonate of potash or soda; the mixture is placed in a platinum* crucible, and maintained at a temperature sufficiently high for fusion, for half an hour. When cold, the mass is reduced to powder, and digested in hot water, and the solution is filtered.

The aqueous solution which passes through the filter contains a combination of potash or soda with the acid previously contained in the

* If the substance possesses the characters of chloride of silver, a crucible of porcelain must be substituted for one of platinum. Chloride of silver is fusible in the flame of the ordinary spirit lamps, and is blackened by hydrosulphate of ammonia. If the substance is supposed to be sulphate of lead (which is also blackened by hydrosulphate of ammonia), the absence of all organic matter must be carefully secured by calcination in a vessel of porcelain, else the platinum crucible may be destroyed.

insoluble substance, together with the excess of alkaline carbonate, and in a few cases some caustic alkali. It may also contain a little chromic acid, if oxide of chromium was present in the original substance, and likewise some peroxide of tin.

1. *Oxide of chromium.*—The presence of chromic acid in the aqueous solution is at once perceived by its yellow colour. As confirmatory tests apply sulphuric acid in excess to a portion of the liquid, to ascertain whether it acquires an orange colour; and boil another portion with hydrochloric acid and alcohol. (See page 115.) The chromic acid, in such a case, is probably derived from the insoluble modification of oxide of chromium, a portion of which was converted into chromic acid by the oxygen of the air, under the influence of the alkaline carbonate, but the greater part of which may be found upon the filter as a green powder.

2. *Silicic acid.*—A portion of the aqueous solution is mixed with excess of hydrochloric acid, and evaporated to dryness: if the dry residue does not completely dissolve in water or dilute hydrochloric acid, silicic acid is present. If fusion with an alkaline carbonate rendered the original substance wholly soluble in water, the substance under examination is silicic acid; but if an insoluble residuum is left, the substance may have been a silicate of some base.

3. *Sulphuric acid*, and

4. *Chlorine.*—Two other portions of the aqueous solution are supersaturated with nitric acid, and tested, one for sulphuric acid, and the other for chlorine, in the usual way, that is, with a salt of barytes and a salt of silver. (pp. 132. 141.)

5. *Peroxide of tin*, and

6. *Arsenic acid.*—If the solution after supersaturation with hydrochloric acid gives a yellow precipitate with sulphuretted hydrogen, either peroxide of tin or arsenic acid may be present. Another portion of the solution supersaturated with hydrochloric acid, is mixed with ammonia in excess: if a white precipitate appears, peroxide of tin is present; but if no precipitate appears, arsenic acid is present. These results should be confirmed by blowpipe experiments, both on the original substance and on the yellow precipitate produced by sulphuretted hydrogen. (See the chapter on Blowpipe Analysis, and also p. 108.)

The portion of the fused mass insoluble in water, and now on the filter, must be well washed with pure water before it is subjected to further examination. If it has the appearance of a metallic globule, it may be *silver*, the original substance being chloride of silver. To determine this point, the metallic globule is dissolved in nitric acid, and subjected to the usual test for silver, namely, hydrochloric acid. (See page 97.)

If the substance on the filter is a green powder, it may be *oxide of chromium*, in which case chromic acid has already been detected in the alkaline solution. As a further confirmation of this result, a little of the green powder may be heated before the blowpipe with borax. (See the chapter on Blowpipe Analysis.)

If the substance on the filter is neither metallic silver nor oxide of

chromium, it is dissolved in hydrochloric or weak nitric acid, after having been well washed, and the solution is treated with sulphuretted hydrogen, hydrosulphate of ammonia, &c., precisely according to the course prescribed in the preceding Section. The base most likely to be present in the nitric acid solution, is either barytes, lime, lead, strontian, or peroxide of tin.

2. If the substance is not rendered soluble in water or acids by fusion with carbonate of potash or soda, it should next be subjected to the action of caustic potash (*potassa fusa*), in a similar manner, a crucible of silver being substituted for one of platinum. The temperature, in this case, should not be allowed to rise above dull redness, to avoid the risk of melting the crucible. The resulting mass is digested in water, and treated in the same manner as if an alkaline carbonate had been employed, instead of a caustic alkali.

3. *Peroxide of iron* is sometimes met with in nature in a state insoluble in acids, and not capable of being rendered soluble in acids by calcination with an alkali. If the substance under examination is of this nature, and resembles native peroxide of iron in appearance, it may be mixed with powdered charcoal, and the mixture strongly heated in a Hessian crucible. The oxide of iron is thereby reduced to the state of metallic iron, which may be dissolved by hydrochloric acid. The presence of iron is then detected in the hydrochloric solution by the usual tests, ammonia (page 59.), and the prussiates of potash. (pp. 67, 68.)

CHAPTER II.

QUALITATIVE ANALYSIS OF A COMPOUND WHICH MAY
CONTAIN ALL THE BASES AND ACIDS IN THE LIST,
PAGE 167.

SECTION I.

QUALITATIVE ANALYSIS OF A COMPLEX SUBSTANCE SOLUBLE IN WATER,
THE CONSTITUENTS OF WHICH ARE INCLUDED IN THE LIST AT
PAGE 167.

WITH complex substances, the examination is to be conducted as if the compound really contained all the ingredients of which it might possibly be composed; and when a reagent does not produce a precipitate, the solution is then to be treated in the same manner as if a precipitate had been formed, and separated from the liquid by filtration. It is of the highest importance, in the qualitative analysis of mixed bodies, that every reagent which is found to produce a precipitate be applied in sufficient quantity to throw down completely the whole of the substance it is capable of precipitating, otherwise the action of the remaining reagents will be materially interfered with.

Frequent advantage will be taken of a tabular method of exhibiting at one view the course of an analysis, by means of brackets, under the opposite arms of which will be mentioned the two results which are commonly afforded by the application of a reagent, namely, the precipitate and the remaining solution. The precipitate is mentioned at the left-hand, and the remaining solution at the right-hand arm of the bracket. In the analysis of mixed compounds, the precipitate and the solution are generally separated by filtration, and each examined apart by other tests, the results which can be produced by these being, as before, mentioned under the opposite arms of brackets.

(A). *Detection of Bases.*

For determining the bases contained in a complex substance, most of the operations are performed upon the same quantity of the original solution, instead of upon several small portions, as recommended when the subject of examination is supposed to consist of only one acid and one base. The quantity of material to operate upon should therefore not be very inconsiderable; but, in general, only a small portion need be reserved for special tests for bases. Enough must be kept, however, for the detection of the acids of the substance.

1. To the aqueous solution of the substance, add a small quantity of hydrochloric acid. If a precipitate appears, continue the addition of the hydrochloric acid, until a precipitate is no longer formed, and the liquid has a decided acid reaction, and then filter the mixture.

a. If the liquid does not exhale the odour of sulphuretted hydrogen, on the addition of hydrochloric acid, the precipitate produced by hydrochloric acid may consist of *chloride of silver*, *chloride of lead*, and *subchloride of mercury*. The liquid which first passes through the filter is preserved for further operations, and the precipitate on the filter is well washed with water. As chloride of lead is slightly soluble in water, it may be removed by washing; but the quantity of lead remaining in the liquid which first passes through the filter is sufficient for the subsequent detection of that metal. The precipitate on the filter is washed with ammonia, so long as any portion of it is dissolved by that liquid.

Chloride of lead remains unaltered by ammonia, but subchloride of mercury is converted into the insoluble black suboxide of mercury. If the precipitate on the filter, therefore, changes from white to black or grey by the application of ammonia, the presence of suboxide of mercury may be inferred; but if it did not darken in colour by ammonia, it consists of chloride of lead. If the presence of silver has been detected, wash away the ammoniacal liquid from the precipitate on the filter completely, then continue the washing, and test the liquid which passes through the filter for lead by sulphuretted hydrogen. (page 79.)

Chloride of silver, if present, is dissolved by the ammonia, and may be reprecipitated from this ammoniacal solution by nitric acid. If an excess of nitric acid produces no precipitate, silver is not present.

b. If the liquid exhales the odour of sulphuretted hydrogen on the addition of hydrochloric acid, and yields a precipitate at the same time (in which case the original liquid would have an alkaline reaction)

the precipitate may consist of sulphur from an alkaline persulphuret, together with the sulphurets of tin, gold, antimony and arsenic ; in which case, the substance under examination contains double sulphur salts, or soluble combinations of the above metallic sulphurets with alkaline or earthy sulphurets. Excepting in the presence of arsenic, such a mixture as this is, in fact, supposed to be obtained in a subsequent part of the examination, by treating the precipitate produced by sulphuretted hydrogen with hydrosulphate of ammonia or potash ; and the remaining steps of the analysis are the same in both cases, the intermediate operation of exposure to sulphuretted hydrogen being neglected. The presence of *arsenic* in the precipitate produced by hydrochloric acid must, however, be determined by the reduction-test described at page 108. Alumina and oxide of chromium should also be sought in the liquid by the usual tests (pp. 64, 65.), after supersaturation with hydrochloric acid.

2. Through the solution acidified by hydrochloric acid, and filtered, if a precipitate was produced by hydrochloric acid, sulphuretted hydrogen gas is next passed, until the liquid smells strongly of sulphuretted hydrogen, after agitation. If a precipitate is produced, pass the liquid through a filter, and reserve it for subsequent operations (3.), and wash the precipitate on the filter with water, until all soluble matter is removed.

The precipitate produced by sulphuretted hydrogen is either sulphuret of arsenic only (produced from arsenious or arsenic acid), in which case its colour is clear yellow, or it may contain all the sulphurets corresponding to the oxides of Class I. (p. 167.), together with sulphur produced from the decomposition of sulphuretted hydrogen by peroxide of iron.

a. If the colour of the precipitate produced by sulphuretted hydrogen is clear yellow, a portion of it is dried and subjected to the reduction-test for *arsenic* described at page 108. If arsenic is found to be present, no bases except the alkalis need be sought for, since the compounds of all other bases with the acids of arsenic are not freely soluble in water : the filtered liquid is then evaporated to dryness, and tested for the alkalis in the usual way. (page 191.)

b. If a yellow precipitate is produced by sulphuretted hydrogen which does not contain arsenic, which fuses at a moderate heat, burns with a blue flame, and volatilizes without residuc, the precipitate is nothing more than *sulphur* (see the note at page 41.), and the precipitate need be examined no further.

c. If the colour of the precipitate produced by sulphuretted hydrogen is not clear yellow, but black, brown, or orange, or if it is yellowish, but has been found to contain *no* arsenic, or something besides sulphur, it is subjected to the course of operations noted in the following Table : —

After having been washed quite clean with water, the precipitate is removed from the filter into a porcelain basin, and digested, with the aid of heat, in hydrosulphate of ammonia containing a little excess of sulphur. If copper is present (as may be ascertained by applying an excess of ammonia to a small portion of the original solution, page 78.), a solution of sulphuret of potassium should be used, instead of hydrosulphate of ammonia. After digestion for a quarter of an hour, if the whole of the precipitate is not dissolved, pour the mixture upon a filter.

The sulphurets which may remain undissolved are those of cadmium, lead, bismuth, copper, and mercury (all of a black colour, except sulphuret of cadmium, which is yellow). Wash the precipitate well upon the filter with water, remove as much as possible from the filter, digest it in strong nitric acid, and apply heat. A small basin may be used in this operation. Sulphur then separates, of a yellow colour, and slowly dissolves if the action of the nitric acid is prolonged. If lead is present, a precipitate of sulphate of lead may be formed on the solution of the sulphur. Lead is therefore to be sought both in the liquid and in the undissolved matter. In general, ten minutes is a sufficient time for the digestion of the sulphurets in nitric acid. The acid liquid is then diluted with a little water, and if necessary passed through a filter.

The undissolved matter may consist of sulphuret of mercury (from the protoxide), sulphate of lead and sulphur.

Heat one portion strongly in a hard glass tube: sulphur and sulphuret of mercury sublime, and sulphate of lead remains behind, as a white powder, which is blackened by hydrosulphate of ammonia, and fuses before the blowpipe.

Mix the other portion with carbonate of soda, and heat the mixture strongly in a glass tube, sealed at one end. *Mercury*, if present, sublimes and condenses on the tube as a white powder, which runs into drops on being stirred (page 94.).

Sulphuret of gold and sulphur remain undissolved. This residue is digested in aqua regia, the solution is evaporated, then diluted and tested for gold with protochloride of tin (page 85.).

The filtered liquid contains tin and antimony, if present in the original substance. Concentrate this solution by evaporation, and pour a small portion of it into water. The formation of a white precipitate indicates the presence of antimony. In the remainder of the solution is placed a clean piece of metallic zinc to precipitate tin and antimony in the metallic state. The precipitate is collected on a filter, washed, and boiled in strong nitric acid, whereby peroxide of tin and antimonious acid are formed (both insoluble). The nitric acid is expelled by evaporation, the residue washed and digested in a solution of bitartrate of potash, which dissolves antimonious acid, but not peroxide of tin. The former is recognised in the liquid by sulphuretted hydrogen, and the latter is reduced before the blowpipe with carbonate of soda on charcoal. To perceive the reduced tin, the heated mass should be levigated with water, in an agate mortar. To ascertain whether the substance contains any tin as *protoxide* (in which case gold cannot be present), test the original solution with chloride of gold (page 98.). See the blowpipe tests for antimony and tin.

A white precipitate by carbonate of ammonia indicates the presence of *cadmium*. Confirm this result by the blowpipe test for cadmium.

If the liquid is blue, *copper* is present.

3. After exposure to sulphuretted hydrogen, and filtration (if a precipitate was thereby produced), the liquid is treated in the following manner. To a small portion of it, ammonia is first added, until the liquid is slightly alkaline to test-paper, and then hydrosulphate of ammonia is applied. The formation of a precipitate indicates the presence of one or more of the bases in Class II. (page 167.) If a precipitate is produced, the whole of the liquid is treated in the same way, some muriate of ammonia being added, if only a very little free hydrochloric acid is present. The mixture is then thrown upon a filter, the precipitate washed and further examined as follows: —

After being well washed, the precipitate is digested in weak aqua regia, with the aid of heat. When the solution is complete, or nothing more than sulphur remains undissolved, the liquid is diluted, filtered if necessary, and a portion of it is then mixed with *excess* of ammonia.

a. If a precipitate is thereby produced, the whole of the liquid is mixed with excess of ammonia, warmed and thrown upon a filter. If much of the acid had been previously expelled by evaporation, it is necessary to add some muriate of ammonia to the solution before adding ammonia. The precipitate on the filter is well washed with water; it may consist of peroxide of iron, oxide of chromium, and alumina.

Redissolve the precipitate in a little hydrochloric acid, and to that solution add an *excess* of cold caustic potash.

Peroxide of iron remains undissolved; redissolve it in hydrochloric acid and test the solution with yellow prussiate of potash. (page 67.) To ascertain whether the original solution contains iron in the state of peroxide or protoxide, or both, apply to it the tests of yellow and red prussiates of potash. (pp. 67, 68.)

Oxide of chromium and alumina are dissolved. If oxide of chromium is present, the solution has a green tinge. On boiling the liquid for a considerable time, oxide of chromium is precipitated, and may be recognised by its blowpipe characters.

If alumina is present, the solution filtered from the precipitate of oxide of chromium gives a precipitate of alumina when mixed with an excess of muriate of ammonia.

b. If a precipitate is produced by ammonia in the acid solution of the sulphurets, the liquid filtered from that precipitate is mixed with hydrosulphate of ammonia till no further precipitate appears; the precipitate thus produced is collected on a filter, well washed, and dis-

solved in aqua regia. The subsequent treatment of this solution is precisely the same as that of the portion of the acid solution of the sulphurets not mixed with ammonia, when that alkali was found to produce no precipitate in the acid solution. The metals which may be present in either case are, manganese, zinc, cobalt, and nickel. The solution is mixed with an excess of caustic potash, the mixture heated, and if necessary filtered.

Oxides of manganese, cobalt, and nickel may remain undissolved. Wash the precipitate well with water, and then digest it with heat, in a mixture of ammonia and carbonate of ammonia.

Oxide of manganese remains undissolved. Confirm this indication of the presence of manganese by the blowpipe tests for that metal.

The ammoniacal solution may contain cobalt and nickel. Evaporate the solution to dryness, and test a portion of the residue for *cobalt* before the blowpipe with borax. To the remainder of the dry mass add a little hydrochloric acid, again evaporate to get rid of most of the excess of acid, redissolve the residue in water, and add to the solution cyanide of potassium, until the precipitate at first formed is completely re-dissolved. If *nickel* is present, this solution affords a precipitate when mixed and heated with dilute sulphuric acid. The precipitate, however, may be produced very slowly. (See the description of such a process as this for the quantitative separation of cobalt from nickel.)

Oxide of zinc may be dissolved. Sulphuretted hydrogen causes a white precipitate of sulphuret of zinc, if that metal is present. Confirm the result by heating either the precipitate or a portion of the original substance with carbonate of soda on charcoal, before the blowpipe.

4. The next subject for examination is the liquid filtered from the precipitate produced by hydrosulphate of ammonia; or if that reagent produced no precipitate, the portion of the liquid filtered from the precipitate produced by sulphuretted hydrogen, which was not mixed with hydrosulphate of ammonia. This liquid may contain the bases in Class III. (p. 167.)

After having ascertained that the liquid does contain some fixed base in solution (by evaporating a few drops to dryness, on a piece of platinum foil, and heating the residue to redness), the liquid is boiled to expel sulphuretted hydrogen, being first, however, mixed with a slight excess of hydrochloric acid when it contains hydrosulphate of ammonia.

Having been boiled until the odour of sulphuretted hydrogen is no longer perceptible, the liquid is mixed with muriate of ammonia (unless that salt has already been formed in the liquid by the decomposition of hydrosulphate of ammonia by hydrochloric acid, in which case its addition is unnecessary), and with a mixture of carbonate of ammonia and caustic ammonia. This mixture is boiled for some time, and if a precipitate is produced, filtered.

a. The precipitate may consist of lime, barytes, and strontian. Dissolve it in as small a quantity as possible of hydrochloric acid, and divide the solution into three portions : —

1. To one portion of the solution add sulphate of soda so long as a precipitate is produced, and then filter. If the filtered liquid, after being neutralized with ammonia, gives a precipitate with oxalate of ammonia, *lime* is present.

2. To another portion add a solution of sulphate of lime : if a *immediate* precipitate appears, *barytes* is present.

3. The other portion of the hydrochloric solution is evaporated to dryness, and the residue treated with strong alcohol. The alcoholic liquid, which may contain both strontian and lime, is filtered, if it leaves anything undissolved, and a few drops are inflamed on the extremity of a glass rod. The presence of *strontian* is indicated by the crimson colour of the flame, and should always be confirmed by evaporating the remainder of the alcoholic liquid to dryness, dissolving the residue in water, and mixing it with a solution of sulphate of lime, which should slowly produce a precipitate of sulphate of strontian (page 52). Lime and strontian are also conveniently distinguished from each other by oxalic acid. The first addition of that acid to a solution of lime and strontian produces a mixed precipitate of oxalate of lime and oxalate of strontian ; but on applying an excess of oxalic acid, the latter is dissolved, while the former remains undissolved. The presence of strontian is detected in the liquid, after filtration, by the application of sulphate of soda.

b. The ammoniacal liquid, filtered from the precipitate of lime, strontian, and barytes, may contain magnesia, potash, soda, and lithia. Before proceeding with the examination of this liquid, however, it is advisable to ascertain whether the whole of the barytes, strontian, and lime is removed from it, by testing one small portion with oxalate of ammonia, and another with sulphate of soda : if either of these reagents produces a precipitate, the remainder of the ammoniacal liquid is boiled with a fresh addition of carbonate of ammonia and ammonia.

To a small portion of the filtered ammoniacal liquid, which should not be very strong, a solution of phosphate of soda is added, and the mixture is well stirred. If a precipitate appears, *magnesia* is present ; in which

case, the subsequent operations for the detection of the fixed alkalies are as follow : —

The remainder of the ammoniacal liquid (that not mixed with phosphate of soda) is evaporated to dryness, and the residue heated to redness in a porcelain or platinum crucible. The mass is then re-dissolved in a small quantity of water, and mixed with a strong solution of either sulphuret of barium or caustic barytes. After a short digestion, pour the mixture upon a filter.

Magnesia is precipitated.

Sulphuric acid is added to the filtered liquid, in order to remove all the barytes; the liquid is boiled, filtered, and then evaporated to dryness. The residue is calcined, re-dissolved in water, and the solution is divided into four portions, which are tested for the fixed alkalies, thus :

1. One portion is tested for *potash* with excess of tartaric acid, and another for the same alkali with chloride of platinum. (page 48.)
2. Another portion is tested for *lithia* with phosphate of soda and ammonia. (page 50.) Soluble salts of lithia communicate a crimson colour to flame.
3. The other portion is tested for *soda* by the ammoniate of potash. (page 49.) A few drops are evaporated to dryness, and the residue tested for soda by the blowpipe flame, to which they communicate a strong yellow colour.

If the phosphate of soda test indicates the absence of magnesia in the above ammoniacal liquid (that filtered from the precipitate of lime, strontian, and barytes), the application of sulphuret of barium or caustic barytes is unnecessary. The liquid is then simply evaporated to dryness, the residue calcined, redissolved in water, and tested for the three fixed alkalies as above.

5. The only base in the list which is not detected in the preceding course of operations is *ammonia*. The presence of this alkali is discovered by applying caustic potash in excess to the original solution, and gently warming the mixture, on which the odour of ammonia is disengaged if that alkali is present. To detect small traces of free ammonia, a piece of moistened red litmus, or a glass rod moistened with hydrochloric acid, may be held over the mixture. The former acquires a blue colour, which vanishes on gently warming the paper: the latter gives rise to white fumes, consisting of muriate of ammonia.

(B). *Detection of the Acids in a complex substance, soluble in water, the constituents of which are included in the list, page 167.*

The various bases contained in the substance having been discovered, a fresh portion of the original solution is submitted to the course of operations noted in the following Table for the detection of the acids which may be present. It will be perceived that all the acids which a substance can contain are arranged into three classes: — 1st, those which are precipitated from a neutral solution by nitrate of barytes; 2nd, those which are not precipitated by nitrate of barytes, but are precipitated by nitrate of silver; and, 3rd, those which are not precipitated either by nitrate of barytes or by nitrate of silver.

If the substance is found to contain other bases than the fixed alkalies, several of the acids enumerated at page 167. need not be sought, since they do not form with such bases compounds soluble in water. If the liquid under examination contains an ammoniacal salt, or is very dilute, boracic, arsenious, and arsenic acids may not be precipitated by nitrate of barytes. These acids are precipitated, however, by the reagent next applied, nitrate of silver; and as their silver compounds are soluble in ammonia, they are afterwards obtained together with chloride of silver, if present. In the Table, the above acids are, therefore, supposed to be contained both in the precipitate produced by nitrate of barytes and in the liquid filtered from that precipitate.

First, examine the action of the liquid under examination on test-paper.

5. *If the liquid has an alkaline reaction*, it may contain alkalies or alkaline earths in the caustic state, or as sulphurates or carbonates, and alkalies in the state of silicates. To a portion of the liquid apply hydrochloric acid, until *peritect neutrality* is obtained, the liquid being warm. *Effervescence* on the addition of hydrochloric acid may proceed from carbonic acid and sulphurous acid or sulphuretted hydrogen. The presence of the latter is detected by its odour and blackening action on a piece of paper impregnated with a salt of lead. If the disengaged gas is inodorous, it consists of *carbonic acid* only; but whether the gas is inodorous or not, the presence of carbonic acid may be determined with certainty by conducting the gas through a little lime-water (see p. 123). If sulphurous acid is present, enough remains in the liquid for detection, provided the neutralization with hydrochloric acid has been conducted with great care. (Carbonic and sulphurous acid gases may be separated from each other by peroxide of lead, which absorbs the latter, but not the former.) If hydrochloric acid produces a precipitate in the liquid, boil the mixture until the sulphuric acid and odour of sulphuretted hydrogen (if present) is no longer perceptible, filter it, wash the precipitate, dry it, and apply heat to it; it fuses, and burns completely away; the residue appears, which may be silicic acid, for which it should be examined by the blowpipe. The examination of the neutral, filtered liquid is conducted as follows:

6. *If the liquid has an acid reaction*, it should be ascertained, by the method described at p. 166, whether this acid reaction is owing to the presence of a neutral metallic salt, which affects test-paper in the manner of a free acid, or to a free acid. If to the former, the further examination is conducted as if the liquid had been neutral to test-paper; but if the liquid contains a free acid, it is rendered exactly neutral with caustic potash.

6. *If the liquid has an acid reaction.* It should be ascertained, by the method described at p. 166, whether this acid reaction is owing to the presence of a neutral metallic salt, which affects test-paper in the manner of a free acid, or to a free acid. If to the former, the further examination is conducted as if the liquid had been neutral to test-paper; but if the liquid contains a free acid, it is rendered exactly neutral with caustic potash.

c. *If the liquid is perfectly neutral*, it contains neither carbonic acid nor sulphureted hydrogen, except small quantities in the free state (see p. 123. and p. 150.). A neutral solution of nitrate of barytes is added to the neutral and strong solution of the substance so long as a precipitate is produced: the mixture is well stirred, poured upon a filter, and the precipitate on the filter is slightly washed with water.

Acids precipitated—sulphuric, arsenic, arsenious, iodic, boric, phosphoric, hydrofluoric, phosphoric, and silicic. Digest the precipitate with concentrated hydrochloric acid. If *sublimous acid* is present, its odour is now perceived: confirm this by applying to a portion of the hydrochloric solution the test of iodine acid and starch (p. 133). Evaporate the remainder of the hydrochloric solution to complete dryness, pour hydrochloric acid upon the dry residue, completely dilute, and filter.

Silicic acid and sulphate of barytes Filter the acid solution, and expose it to sulphuretted hydrogen gas.

(indicating *sulphuric acid*) re-precipitated — sulphuric acid, a mixture of arsenic and phosphoric acids, and from *arsenious* and *arsenic acid*; and iodine, from *iodic acid*. The iodine is afterwards re-precipitated by dissolved as hydriodic acid, is the best activator for arsenic by the reduction-t- $\text{st.p. } 104^{\circ}$. Final solution, mixed with excess of hydrochloric acid leaves, on evaporation to dryness, a white residue insoluble in hydrochloric acid, as a precipitate, a white residue insoluble in hydrochloric acid, as a precipitate, *sillicic acid* is also

Acids not precipitated by nitrate of barytes — hydrochloric, hydriodic, if the liquid is very dilute, or contains an ammoniacal salt, arsenic, add to the liquid a solution of nitrate of silver, so long as a precipitate forms.

Add excess of ammonia to the precipitate, and filter, if it is not wholly dissolved.

iodide of silver, of a yellowish colour, remains undissolved. The precipitate is a solution of silver chloride with free chlorine and starch mucilage as described at page 148.

Acids not precipitated.—To *nitric* and *chlorotic*. To detect *nitric* acid, apply to the original solution to the tests of sulphuric acid with copper filings, and sulphuric acid with protosulphate of iron (p. 185.). If *chlorotic* is present, the dry substance, when heated, gives off oil of vitriol, disengages a bleaching vapour, which colours vegetable colouring-matters; and the liquid in which it is dissolved, and the liquid of silver protosulphate, produces no precipitate, leaves, on evaporation, to dryness, and calcination, a white residue, which is rich in silver, which is recognised by its insolubility and fusibility.

SECTION II.

QUALITATIVE ANALYSIS OF A COMPLEX SUBSTANCE, INSOLUBLE IN WATER, BUT SOLUBLE IN NITRIC ACID, HYDROCHLORIC ACID, OR AQUA REGIA, THE CONSTITUENTS OF WHICH ARE INCLUDED IN THE LIST AT PAGE 167.

(A). *Detection of Bases.*

If the substance is dissolved in *nitric acid*, add a little hydrochloric acid to the solution. If a white precipitate is formed by hydrochloric acid, not readily soluble in an excess of that acid, lead, silver, and mercury (as suboxide) may be present. Collect the precipitate on a filter (after dilution of the liquid), wash it with water, and examine it by ammonia in the manner described at page 185. The filtered liquid is then exposed to sulphuretted hydrogen.

If the substance is dissolved in *hydrochloric acid* or *aqua regia*, it contains neither oxide of silver nor suboxide of mercury. Oxide of silver is almost perfectly insoluble in both of these acids: suboxide of mercury is insoluble in hydrochloric acid, but dissolves in *aqua regia*, with conversion into protochloride of mercury.

If much free acid is present in the liquid, the principal part of it should be removed by evaporation nearly to dryness: the residue is then mixed with water. A milkiness on dilution may proceed from the presence of bismuth or antimony, but this may generally be disregarded, and the examination be continued as if no milkiness had occurred.

1. Through the diluted acid solution (filtered from the precipitate produced by hydrochloric acid) sulphuretted hydrogen gas is passed until the liquid smells strongly of sulphuretted hydrogen, after agitation and warming. If a precipitate is thereby produced, the liquid is passed through a filter, and reserved for subsequent examination (2.); and the precipitate on the filter is washed until all soluble matter is removed.

The precipitate may contain the sulphurets of all the metals of Class I. (p. 167.), together with the two sulphurets of arsenic derived from ar-

senious and arsenic acids, and sulphur derived from the decomposition of sulphuretted hydrogen by peroxide of iron. Excepting in the possible presence of arsenic, this mixture differs in no respect from that supposed to be precipitated by sulphuretted hydrogen from the acidified solution of a substance soluble in water: its further examination is therefore conducted according to the Table at p. 187., with one only additional operation. A portion of the precipitate produced by acetic acid in the solution of the sulphurets in hydrosulphate of ammonia or sulphuret of potassium is subjected to the reduction-test for arsenic described at page 108.

2. After exposure to sulphuretted hydrogen and filtration, if a precipitate was thereby produced, a small portion of the liquid is rendered slightly alkaline by ammonia, and then mixed with hydrosulphate of ammonia. If a precipitate is thereby formed, the whole of the liquid is treated in the same way, and poured upon a filter. The precipitate is washed, and further examined as follows, and the liquid which passes through the filter is reserved for subsequent examination. according to the course prescribed for a similar liquid in the preceding section, page 189. (4.)

If the substance under examination is soluble in water, the precipitate produced by hydrosulphate of ammonia would contain no other metals or bases but those of Class II. (p. 167.); but as the substance now under consideration is insoluble in water, this precipitate may also contain certain salts of lime, barytes, magnesia, and strontian, insoluble in water, but soluble in acids. The course of operations to which the precipitate is subjected is exhibited in the following Table:—

After being well washed, the precipitate is digested in weak aqua regia, with the aid of heat. When the solution of the precipitate is complete, or nothing more than sulphur remains undissolved, the liquid is diluted, filtered if necessary, and a portion of it is then mixed with excess of ammonia. If much of the acid has been expelled by evaporation, it is necessary to add some muriate of ammonia to the solution before adding ammonia. If a precipitate is produced by ammonia insoluble in excess, the whole of the liquid is mixed with excess of that alkali, warmed, and poured upon a filter.

The precipitate may consist of peroxide of iron, oxide of chromium, alumina, and phosphates and borates of lime, magnesia, strontian, and barytes. Wash the precipitate with water, remove it from the filter, and digest it in a dilute solution of caustic potash. If the precipitate is in too small a quantity to be easily removed mechanically from the filter, a little hydrochloric acid may be poured upon the filter, and this acid solution mixed with excess of caustic potash.

The filtered liquid may contain oxides of manganese, cobalt, nickel, and zinc. For the treatment of this solution, or (in case ammonia produced in the acid solution of the sulphurets no precipitate insoluble in excess of ammonia) for the treatment of the portion of the acid solution not mixed with ammonia, see pp. 188, 189, *b*.

Peroxide of iron and the phosphates and borates of the alkaline earths may remain undissolved. Collect this residue on a filter, wash it well, and dissolve it in a little hydrochloric acid. Test a small portion of this solution for *peroxide of iron* with the yellow prussiate of potash (page 67.). To the remainder of the hydrochloric acid solution add, first, a tolerably large quantity of perchloride of iron, and then ammonia, until a slight alkaline reaction on test-paper appears; the mixture being well stirred. Pour the mixture upon a filter.

Oxide of chromium and alumina are dissolved. For the manner of detecting and distinguishing these bases in an alkaline liquid, see page 188.

Peroxide of iron and phosphate of the peroxide of iron are precipitated.

The filtered liquid may contain lime, magnesia, strontian, and barytes. Having ascertained that the liquid does contain some fixed base in solution (by evaporating a few drops to dryness on a piece of platinum foil, and heating the residue to redness), the liquid is mixed with ammonia and carbonate of ammonia, and boiled for some time. If a precipitate is thereby produced, the mixture is poured upon a filter.

Lime, barytes, and strontian may be precipitated. For the detection and separation of these earths in the precipitate, see page 190. *a*.

The filtered ammoniacal liquid may contain *magnesia*; in which case it gives a white crystalline precipitate when mixed with phosphate of soda (page 54.).

(B). *Detection of the Acids in a complex substance, insoluble in water, but soluble in acids, the constituents of which are included in the list, page 167.*

As all chlorates are soluble in water, *chloric acid* need not be sought for. *Arsenious* and *arsenic acids*, if present, have already been detected in the examination for bases.

1. A portion of the substance is mixed with concentrated hydrochloric acid. Effervescence indicates the presence of a carbonate, a sulphite, or a sulphuret, decomposable by hydrochloric acid. The hydrochloric acid solution may contain phosphoric, sulphuric, iodic, and silicic acids.

a. Carbonic acid, sulphurous acid, and sulphuretted hydrogen. If the evolved gas is inodorous, it consists of carbonic acid only. In a mixture of sulphurous acid and carbonic acid gases, the former is recognised by its odour, and the latter by its action on lime-water. (See page 123., and the remarks at the beginning of the Table, p. 193.) In a mixture of carbonic acid and sulphuretted hydrogen gases, the former may also be recognised by its action on lime-water, and the latter by its odour, and action on salts of lead. (page 150.) Sulphurous acid and sulphuretted hydrogen mutually decompose each other, with formation of water and sulphur, and are therefore not evolved together. If one of these gases is disengaged in excess, its odour is of course perceived. When a mixture of a sulphite insoluble in water and a sulphuret is boiled in a solution of an alkaline carbonate, a sulphite of the alkali is formed, and the solution disengages the odour of sulphurous acid, when saturated with sulphuric acid. Iodic acid and starch may also be applied to the neutralized or acidified liquid as a test for sulphurous acid. (page 133.)

b. Phosphoric acid, sulphuric acid, iodic acid, and silicic acid.—These acids, if present, are contained in the solution of the substance in hydrochloric acid. The presence of silicic acid is first ascertained by evaporating the solution to dryness, and digesting the dry mass in hydrochloric acid a little diluted. If *silicic acid* is present, a light white powder remains undissolved. (See page 131.) This residue should be examined before the blowpipe. (See the characters of silicic acid before the blowpipe.)

To a portion of the acid solution filtered from silicic acid, add a few drops of a weak solution of chloride of barium. The production of a white precipitate, which does not disappear either by dilution or by the application of more hydrochloric acid, shows the presence of *sulphuric acid*.

To another portion of the same solution, somewhat diluted, apply a solution of sulphurous acid in water, and some starch mucilage, as a test for *iodic acid*. (See page 125. and also page 148.)

To discover the presence of phosphoric acid, apply to another portion of the hydrochloric acid solution the test of perchloride of iron with ammonia, &c., described at pages 127, 128. (See also the note at page 180., on the manner of detecting phosphoric acid when present as phosphate of alumina.)

2. A portion of the substance is next digested in tolerably strong nitric acid. If the action proceeds slowly, heat may be applied.

Sulphur.—The disengagement of an abundance of red fumes, accompanied by the separation from the substance of a yellowish powder, which aggregates into lumps, and slowly dissolves, indicates the presence of a sulphuret. The acid solution is found to contain sulphuric acid, when considerably diluted and tested with a salt of barytes.

Chlorine.—To discover the presence of a chloride, add a solution of nitrate of silver to the clear nitric acid solution of the substance: if a precipitate is produced, wash it, either by affusion and decantation or by filtration, and digest it in ammonia. If the ammoniacal liquid gives a white precipitate on being supersaturated with nitric acid, the substance contains a chloride.

3. For the detection of *iodine*, *fluorine*, and *boracic acid*, the substance is acted on by concentrated sulphuric acid, in the manner described at page 179.

4. The appearance of deflagration when the substance is placed on a piece of burning charcoal, may arise from either *nitric acid* or *iodic acid*. To detect the former, apply to a portion of the original substance, sulphuric acid and copper filings (page 154.). The latter, if present, has been already detected.

SECTION III.

QUALITATIVE ANALYSIS OF A COMPLEX SUBSTANCE INSOLUBLE OR BUT SLIGHTLY SOLUBLE IN WATER AND ACIDS, THE CONSTITUENTS OF WHICH ARE INCLUDED IN THE LIST AT PAGE 167.

The substances to be here considered are the following:—sulphates of lime, barytes, strontian, and lead; silica and some silicates; chloride of silver; some acid arseniates, after

having been strongly calcined; and the insoluble modifications of oxide of chromium, peroxide of tin, and peroxide of iron.

1. To render the substance soluble, it is first mixed in a state of fine powder, with about three times its weight of dry carbonate of soda; the mixture is introduced into a platinum crucible, and maintained at a temperature sufficiently high for fusion for nearly half an hour. If the presence of chloride of silver is suspected, from the substance being blackened by hydrosulphate of ammonia, and from its comportment before the blowpipe, a crucible of porcelain must be used instead of one of platinum. (See the note at page 181.) But in the absence of metallic compounds easy of reduction, a platinum crucible is decidedly to be preferred. When a crucible of earthenware or porcelain is used, silicic acid, derived from the crucible is always found among the soluble products.

After being cooled and powdered, the fused mass is digested in hot water *until all the soluble matter is dissolved*, and the solution is filtered. This aqueous solution contains the excess of carbonate of soda, together with combinations of soda with the acids previously contained in the insoluble substance, and, in a few cases, a little caustic alkali. If the substance under examination contains oxide of chromium, a little chromic acid will be found in the aqueous solution; and peroxide of tin, if present in the substance, will also be found in the solution.

For the modes of detecting *oxide of chromium* (indicated by the presence of chromic acid in the solution), *silicic acid*, *sulphuric acid*, *chlorine*, *arsenic acid*, and *peroxide of tin*, see page 182.; the same processes being applicable for the detection of these bodies when one only or all are supposed to be present. If a precipitate is produced in the acidified solution by sulphuretted hydrogen, whereby the presence of either arsenic or tin, or both, is indicated, the precipitate should be collected and examined by the test for arsenic described at page 108. Another portion of the aqueous solution is acidified by hydrochloric acid and tested for peroxide of tin by ammonia. (page 182.).

The part of the fused mass insoluble in water is examined

for the various bases which the substance contained. These bases are now either in the free state or as carbonates, and are generally freely soluble in acids.* If chloride of silver was present in the original substance, the residue insoluble in water contains metallic silver, either as a bright metallic globule or in a fine pulverulent state.

This residue is now dissolved in either hydrochloric or nitric acid (the former being preferred in all cases where it effects solution), and the solution is submitted to the regular examination, detailed in the preceding section, for all bases except the alkalies.

The fixed alkalies are often contained in silicates which are insoluble in acids, and which require, therefore, calcination with an alkaline carbonate, or alkaline earth, in order to be rendered soluble. When *alkalies* are sought, in such a case, the silicates should be calcined with carbonate of barytes or of lime, or quick-lime, instead of carbonate of soda. The barytes or lime may be removed from the solution of the ignited mass in an acid by carbonate of ammonia, as an insoluble carbonate: the filtered solution is then evaporated, the residue calcined to expel ammoniacal salts, and dissolved in water. The solution thus obtained is tested for potash by tartaric acid and chloride of platinum; for lithia, by the blowpipe; and for soda, by the blowpipe and antimoniate of potash. For a modification of the above process, see the mode of obtaining the amount of alkalies in silicates not decomposable by acids, under the Quantitative Analysis of Silicates.

2. If the substance is not rendered soluble in water or acids by fusion with carbonate of soda (being carefully washed with water before an acid is applied), it is next treated with caustic potash, as described at page 183. See also, at the same place, the manner of obtaining a solution of the variety of native peroxide of iron which is not directly soluble in acids.

• If the insoluble portion of the fused mass has not been perfectly washed before it is treated with an acid, it may not completely dissolve, owing to the reproduction of the original substance. If the substance contains sulphate of barytes, for instance, and the sulphate of soda present in the fused mass is not completely washed away from the insoluble carbonate of barytes, of course sulphate of barytes will be reproduced on the application of either hydrochloric or dilute nitric acid.

CHAPTER III.

QUALITATIVE ANALYSIS OF A SUBSTANCE WHICH MAY CONTAIN ALL INORGANIC BODIES WHOSE PROPERTIES ARE WELL KNOWN.

SECTION I.

EXAMINATION FOR BASES AND SOME ACIDS.

THOUGH the following course of operations for the qualitative analysis of a highly complicated mixture is adapted to substances soluble and insoluble both in water and acids, yet it is always advisable to examine separately,—1st, that portion of a substance which is soluble in water; 2nd, that which is insoluble or slightly soluble in water, but soluble in acids; and, 3rd, that which is insoluble or slightly soluble in acids. When the analysis is thus conducted, the true constitution of the substance under examination, that is, the mode of arrangement of its various acids and bases, is generally determined with much more precision than when the whole of a substance containing matters soluble and insoluble in water and acids is subjected to the means of effecting solution which should be the last resorted to, namely, fusion with an alkali.

The indications of the presence or absence of various bodies, which are obtained in the following course of analysis, should be rigorously proved by applying, both to the original substance and to the precipitates obtained during the analysis, other tests than those mentioned in the following Tables, namely, the most characteristic of those noticed in the preceding division of this work, on the “Behaviour of Substances with Reagents.”

1. *The substance is soluble in water.* — The strong aqueous solution of the substance is first mixed with *an excess* of

concentrated hydrochloric acid, and heated. The bodies which may be precipitated by hydrochloric acid, and not easily re-dissolved in an excess when the mixture is heated, are, chloride of silver, chloride of lead, subchloride of mercury, silicic acid, tungstic acid, tantalic acid, and titanilic acid.

If the substance under examination is alkaline, and the odour of sulphuretted hydrogen is perceived on supersaturation with hydrochloric acid, the precipitate may consist of sulphur and such metallic sulphurets as form soluble combinations with alkaline sulphurets, namely, the sulphurets of tin, gold, antimony, arsenic, platinum, iridium, molybdenum, tellurium, and selenium. The mode of analyzing such a mixture is exhibited in the Table at page 206.

But when the odour of sulphuretted hydrogen is not disengaged by the addition of hydrochloric acid, the examination of the precipitate may be conducted after the following manner. A portion of the precipitate is digested in ammonia, and the ammoniacal liquid is supersaturated with hydrochloric acid. The formation of a white precipitate, which blackens on exposure to light, shows the presence of *chloride of silver*. To detect *chloride of lead*, a portion of the precipitate, after being well washed, is heated with water, and the liquid tested for lead with sulphuretted hydrogen. (page 79.) If *subchloride of mercury* is present, the precipitate is rendered black, or is darkened in colour, by ammonia, and when mixed with carbonate of soda, and heated to redness in a glass tube, disengages metallic mercury. (See page 94.) *Silicic acid* is recognised by its blowpipe characters, and by the gelatinous appearance which it assumes when its solution is mixed with hydrochloric acid, and evaporated to dryness. (See page 131.) *Tungstic acid* is recognised by its blowpipe characters, and by its solubility in hydrosulphate of ammonia. (See page 111.) *Titanic acid* is distinguished from other bodies by its property of being precipitated from its solution in cold hydrochloric acid by the application of heat (see page 70.), and by its blowpipe characters. *Tantalilic acid* is also recognised by its behaviour before

the blowpipe.* The solution, filtered from the precipitate produced by hydrochloric acid, is then submitted to the course of operations noted in the following Tables.

The disengagement of *chlorine gas*, when the strong aqueous solution of the substance is heated with hydrochloric acid, may proceed from the presence of *chromic acid*, *vanadic acid*, *selenic acid*, *manganic acid*, *hypermanganic acid*, *peroxide of cerium*, or *sesquioxide manganese*. These acids or peroxides are reduced by the hydrochloric acid to a lower state of oxidation, in which state they are afterwards found in the course of the examination.

2. *The substance is freely soluble in hot hydrochloric acid, but insoluble or very slightly soluble in water.*—In that case, the substance contains neither *silver*, *suboxide of mercury*, *tungstic acid*, *tantallic acid*, nor *titanic acid*. *Silicic acid* and a small quantity of *lead* may be present. The former is detected in the usual way, by evaporating to dryness, and treating the dry residue with diluted *hydrochloric acid*. If present, it should be separated from the entire quantity of the solution required for the analysis. Lead, when present, is afterwards detected among the sulphurets precipitated by sulphuretted hydrogen.

The evolution of chlorine during digestion in hot hydrochloric acid may proceed from the presence of *hypermanganates*, *manganates*, *chromates*, *seleniates*, *vanadiates*, and several *metallic peroxides*.

The hydrochloric acid solution, a little diluted, is treated as directed in the following Tables.

3. *The substance is insoluble or slightly soluble in water and hot hydrochloric acid, but soluble in nitric acid.*—The substances

* The following mode of separating titanic acid from tantallic acid is proposed by M. Wöhler. To the mixture of the two acids sugar is added, the mixture is carbonized by heat, then placed in a tube and exposed to a red heat in a current of chlorine gas. Chlorides of tantalum and titanium distil over, and are collected in a vessel containing water. On adding sulphuric acid to the aqueous solution, tantallic acid is precipitated, and titanic acid remains in solution.

which are to be sought for before the solution is submitted to the course of operations noted in the Tables, are, *silver, lead, and mercury in the state of suboxide, and silicic acid*. The presence of one or more of these metals is indicated by the formation of a white precipitate on the application of hydrochloric acid to a portion of the nitric acid solution. (See page 185.) The usual test of evaporation to dryness is resorted to for the detection and separation of *silicic acid*. To ascertain whether the dry residue is wholly soluble in acids, or whether silicic acid remains undissolved, nitric acid should be applied to the residue in cases where hydrochloric acid produces a precipitate in the solution; and after having thus proved the presence or absence of silicic acid, the nitric acid solution is again evaporated to dryness, the residue digested in hydrochloric acid, diluted, and exposed to sulphuretted hydrogen, as directed in the following Table. But if hydrochloric acid produces no precipitate in the nitric acid solution of the substance, the dry residue obtained by evaporating that solution is digested in hydrochloric acid, instead of nitric, diluted, filtered (if silicic acid is present), and exposed to sulphuretted hydrogen.

4. *The substance is insoluble or slightly soluble in water, hydrochloric acid, and nitric acid, but soluble in aqua regia.*—The only preliminary operation on the solution of such a substance in aqua regia is evaporation to dryness, to detect (and separate, if present,) *silicic acid*. The residue of the evaporation is digested in hydrochloric acid, and the solution is diluted, filtered, and exposed to sulphuretted hydrogen, as directed in the Table.

5. *The substance is insoluble or slightly soluble in water and acids.*—If the substance is insoluble both in water, hydrochloric acid, nitric acid, and aqua regia, the usual method of obtaining solution in such a case is to be resorted to, namely, fusion with an alkaline carbonate, or, in some cases, with a caustic alkali. (See pages 181. and 199.) If the substance is to be tested for alkalies, quick-lime is to be used instead of an alkaline carbonate. (See page 200.)

The calcined mass, after being cooled and powdered, is digested in water, and the solution examined in the manner already described, as that of a substance soluble in water. (1.) The part of the fused mass insoluble in water is washed until all soluble matter is removed, and then dissolved in hydrochloric acid, or, if metallic silver is present, in nitric acid. The solution thus obtained is treated precisely as before described; if made in hydrochloric acid, as that of a substance soluble in hydrochloric acid (2.); or, if made in nitric acid, as that of a substance soluble only in nitric acid. (3.)

Through the aqueous solution of the substance acidified by hydrochloric acid, or through the solution of the substance in an acid, transmit sulphuretted hydrogen gas to saturation; allow the liquid to stand for twelve hours, then boil it to expel the excess of sulphuretted hydrogen, and filter. Wash the precipitate with sulphuretted hydrogen water, and digest it, with the aid of heat, in hydrosulphate of ammonia; or in case *copper* is present (which is ascertained by applying excess of ammonia to a portion of the original solution, see page 78.), digest the precipitate in a solution of sulphuret of potassium. After digestion for about a quarter of an hour, collect the undissolved portion on a filter.*

The sulphurets undissolved are those of cadmium, bismuth, lead, copper, mercury, osmium, palladium, and rhodium.

To detect the first five of these metals, proceed according to the Table, page 187.

After the application of sulphuric acid for the detection and separation of lead, and of hydrochloric acid for that of silver, neutralize the filtered solution by carbonate of soda, and add to it a solution of cyanide of mercury; if a white gelatinous precipitate falls, this is cyanide of *palladium*.

Osmium is detected by the fumes of osmic oxide disengaged when the substance is boiled with nitric acid (see page 95.).

To discover the presence of *rhodium*, reduce the substance to the metallic state by heating it in hydrogen gas; metallic rhodium is insoluble in nitric acid and aqua regia, but dissolves in melted bisulphate of potash (see page 96.).

* If the solution of the substance contains arsenic in the state of arsenic acid, and zinc is also present, the precipitate produced by sulphuretted hydrogen in an acid solution may contain zinc in the form of a double sulphuret of zinc and arsenic. But if the solution is exposed to sulphurous acid gas, previous to the treatment with sulphuretted hydrogen, the arsenic acid is reduced to the state of arsenious acid, and sulphuretted hydrogen then precipitates sulphuret of arsenic unaccompanied by zinc, the whole of the latter metal remaining in the acid solution.

The sulphurets dissolved are those of tin, gold, antimony, arsenic, platinum, iridium, molybdenum, tellurium, and selenium. Dilute the solution with a little water, and add to it acetic acid in slight excess. Collect the precipitate then formed on a filter, wash it, and dry it. After having ascertained that this precipitate contains something besides sulphur, examine a portion of it before the blowpipe for *arsenic* (see page 108.), *molybdenum*, and *selenium*. Dissolve the remainder in aqua regia; evaporate off the excess of acid, and add dilute hydrochloric acid. If the absence of selenium has been proved by the blowpipe, and that of gold by protochloride of tin (applied to a portion of the original solution), the production of a black precipitate on adding sulphurous acid to the solution of the sulphurets indicates the presence of *tellurium*. If selenium and gold are also present, then tellurium must be sought by the blowpipe. Add a concentrated solution of chloride of potassium to the above hydrochloric acid solution of the sulphurets.

Precipitated—chloride of platinum and potassium, and chloride of iridium and potassium. Filter; ignite the precipitate with an equal weight of carbonate of potash, wash the mass with water, and treat what remains with hot aqua regia.

Peroxide of *iridium* may remain undissolved. The solution may contain *platinum*: chloride of potassium then produces in it a yellow crystalline precipitate.

A portion of the filtered solution is tested for *gold* with protochloride of tin (see page 89.); the remainder is mixed with an excess of bicarbonate of potash, and the precipitate thereby produced is examined for *tin* and *antimony* by the blowpipe. (See a method of distinguishing between tin and antimony described in the Table, page 187.)

The precipitate produced by sulphuretted hydrogen in an acid solution may contain zinc in the form of a double sulphuret of zinc and arsenic. But if the solution is exposed to sulphurous acid gas, previous to the treatment with sulphuretted hydrogen, the arsenic acid is reduced to the state of arsenious acid, and sulphuretted hydrogen then precipitates sulphuret of arsenic unaccompanied by zinc, the whole of the latter metal remaining in the acid solution.

Treatment of the Solution filtered from the Precipitate produced by Sulphuretted Hydrogen.

Add to it, first ammonia, and then a slight excess of hydrosulphate of ammonia: expose the mixture to the air until the excess of hydrosulphate of ammonia is dissipated; filter, if a precipitate is formed, and wash the precipitate with very dilute ammonia.

Precipitated — sulphurets of zinc, iron, manganese, nickel, cobalt, and uranium; alumina, glucina, thorina, yttria, zirconia, oxide of cerium, oxide of chromium; and if the substance under examination is insoluble in water, certain salts of barytes, strontian, lime, and magnesia. When well washed, dissolve the precipitate in aqua regia, evaporate off the excess of acid, dilute, and add to the solution sulphuric acid mixed with a little alcohol.

Precipitated — sulphates of barytes, lime, and strontian. This precipitate may be calcined with carb. soda, and further treated as described in Chap. II. Sect. III. (page 198.)

Filter the liquid from the precipitate by sulphuric acid, add to it muriate of ammonia, and excess of caustic ammonia.

Digest the precipitate produced by ammonia in cold caustic potash.

Undissolved by potash — perox. of iron, zirconia, thorina, ox. of cerium, yttria, perox. of uranium, phosphate of magnesia. Filter, wash, and dissolve the precipitate in hydrochloric acid, and add to the solution a large excess of bicarbonate of potash.

Undissolved — perox. of iron; (dissolve in hydrochloric acid, and test with pruss. of potash;) phosphate of magnesia; phosphate of yttria. In solution — zirconia, thorina, ox. of cerium, yttria, and perox. of uranium: neutralize the solution by hydrochloric acid, add to it a dilute solution of sulphate of potash, and boil it with caustic potash after standing a few hours.

Zirconia is precipitated. Neutralize the filtered liquid, and add to it excess of a hot saturated solution of sulphate of potash, boil and dilute slightly.

Precipitated — thorina and ox. of cerium; the latter is detected by the blowpipe. In solution — perox. uranium, and yttria; ammonia gives a yellow precipitate of perox. uranium. Confirm this indication by the blowpipe test for uranium.

In solution — zinc, manganese, nickel, cobalt. For the qualitative analysis of such a mixture, see pp. 188, 189, b.

In solution — alumina, glucina, and oxide of chromium; add carbonate of ammonia in excess.

Precipitated — alumina and oxide of chromium; boil the precipitate in a strong solution of carbonate of potash.

Alumina, remains undissolved; confirm this result by the blowpipe, with nitrate of cobalt. Oxide of chromium is dissolved; apply the blowpipe test for this oxide.

In solution — glucina; neutralize the liquid with hydrochloric acid, and add excess of ammonia. (A trace of ox. of chromium may also be precipitated by ammonia.)

SECTION II.

EXAMINATION FOR ACIDS.

The acids to be sought, besides those mentioned at page 167., are the following : —

| | |
|---------------------------|-------------|
| Acetic | Manganic |
| Bromic | Nitrous |
| Chromic | Oxalic |
| Hydrobromic (or bromine) | Phosphorous |
| Hydrocyanic (or cyanogen) | Selenic |
| Hypermanganic | Selenious |
| Hyposulphurous | Tartaric |
| Hyposulphuric | |

The evolution of chlorine, when the substance is digested in hot hydrochloric acid, may proceed from the presence of chromic, chloric, iodic, bromic, selenic, manganic, and hypermanganic acids.

To obtain some indication of the nature of the acids present, for subsequent confirmation, a small portion of the substance, either in the dry state (powdered), or in a strong aqueous solution, is mixed with concentrated sulphuric acid in a test tube. If no action takes place immediately, a gentle heat may be applied. The disengagement of any volatile acid may be perceived by the formation of a white cloud when a glass rod moistened with strong ammonia is held over the tube.

1. *A gas is disengaged which has a strong odour of sulphurous acid.* — If this is the case, a hyposulphite, a sulphite, or a hyposulphate may be present. For the manner of distinguishing between these classes of salts, see pages 133. 151. and 153. If organic matter is present, and heat applied, sulphurous acid may also be produced through the deoxidation of the sulphuric acid.

2. *Coloured gases or vapours are disengaged.* — A reddish vapour may proceed from a bromate, a bromide, or a nitrite. In the cases of a bromate and a bromide, the reddish vapour consists of bromine mixed with oxygen, if a bromate is present, or with sulphurous acid, if a bromide is present. See the characters of bromates (bromic acid) at pages

118. 122., and those of bromides (hydrobromic acid) at pages 136. 145. When sulphuric or other strong acid is mixed with a nitrite, nitric oxide gas is disengaged, which forms ruddy fumes of nitrous acid, by combining with the oxygen of the air. (See the characters of nitrites (nitrous acid), at pages 137. 156.) The evolution of a *yellowish* gas, by sulphuric acid, indicates the presence of a chlorate. (See the characters of chlorates (chloric acid) at pages 136. 138.) A *purple* vapour may proceed from the presence of an iodide. (See the characters of iodides (hydriodic acid) at pages 136. 147.)

3. *Carbonic acid gas is disengaged.*—If unaccompanied by other gases or vapours, carbonic acid may generally be recognised by its freedom from colour and odour; and in the presence of other gases, by the precipitate of carbonate of lime, which it produces when passed through a mixture of a solution of chloride of calcium with ammonia. In the experiment now under consideration, carbonic acid gas may be afforded by a carbonate and by an oxalate. A carbonate yields carbonic acid when mixed with cold, diluted sulphuric acid; but an oxalate yields no carbonic acid gas when treated with cold sulphuric acid, or when the acid is diluted. For the characters of carbonates (carbonic acid), see pages 118. 122.; and for those of oxalates (oxalic acid), see pages 119. 126. If the mixture of the substance with sulphuric acid blackens, other matters may be present which would cause a disengagement of carbonic acid gas.

The other acids volatilized when their compounds with bases are heated with sulphuric acid, are, hydrosulphuric (from certain classes of sulphurets), hydrofluoric (from fluorides), hydrochloric (from chlorides,) nitric (from nitrates), acetic (from acetates), and hydrocyanic (from certain classes of cyanides). The means of detecting all these, except acetic and hydrocyanic, are pointed out in the Table at page 193. and at page 197.

Acetic acid is recognised with certainty by the product of the distillation of the substance with sulphuric acid being capable of dissolving protoxide of lead, thus forming a solution which possesses an alkaline reaction on test-paper, when the oxide of lead is present in excess. (See page 138.) For the manner of detecting *hydrocyanic acid*, or an alkaline or earthy *cyanide*, see page 143.

The acids, or electronegative bodies, which do not volatilize when their combinations with bases are heated with strong sulphuric acid, are arsenic, arsenious, iodic, phosphoric, phosphorous, boracic, sulphuric, silicic, selenious, selenic, and tartaric, and, when united with certain bases, sulphur. The means of detecting each of these bodies, with the exception of selenious, selenic, phosphorous, and tartaric acids, have already been noticed. (See pages 193. 197.)

Selenious and selenic acids.—The presence of selenium having been ascertained by the blowpipe in the course of the determination of the bases, to ascertain whether this element is present in the state of selenious or in

that of selenic acid, the acidified solution of the substance (not boiled with hydrochloric acid) is treated with sulphuretted hydrogen, and the precipitate examined by the blowpipe for selenium. Selenious (but not selenic) acid affords a precipitate with sulphuretted hydrogen. By being heated with hydrochloric acid, selenic acid is reduced to the state of selenious acid, and is then of course precipitated by sulphuretted hydrogen.

Phosphorous acid.—Solutions of phosphites possess the power of reducing salts of mercury and gold to the metallic state, in acid solutions. Most phosphites evolve hydrogen gas, when heated to redness; but some, as well as all *hypophosphites*, evolve phosphuretted hydrogen gas. (See the characters of phosphites and hypophosphites at pages 128, 129.)

Tartaric acid.—If tartaric acid is present, the mixture of the substance with sulphuric acid carbonizes slowly in the cold, and rapidly on the application of heat. In a substance soluble in water, tartaric acid is recognised by the sparingly soluble, white, crystalline precipitate of bitartrate of potash, which falls when a mixture of a strong solution of acetate of potash and free acetic acid is added to the strong aqueous solution of the substance. (See pages 120, 134.) The peculiar comportment of tartrate of lime (produced on adding a solution of a tartrate to lime-water or a mixture of solution of chloride of calcium with ammonia) with caustic potash may also be taken advantage of as a good test for tartaric acid. (See the note at page 135.)

After treating the substance with strong sulphuric acid, as a means of preliminary examination, it should in the next place be subjected to a systematic course of experiments after the plan prescribed in the Table at page 193., or in the section following that table, according to whether the substance is soluble or insoluble in water.

1. *The substance is soluble in water.*—The action of the solution on test-paper having been ascertained, and the presence or absence of a carbonate, a sulphite, and a sulphuret determined in the manner directed in the Table at page 193., a solution of nitrate of barytes is added to the strong and neutral solution of the substance: if a precipitate is produced, the mixture is well stirred, poured upon a filter, and the precipitate on the filter is slightly washed with water.

Besides the acids mentioned at page 193., a salt of barytes may precipitate chromic acid, oxalic acid, tartaric acid, bromic acid, phosphorous acid, selenic acid, and selenious acid.

The presence of a neutral *chromate* is easily recognised by the yellow colour of the original solution, by its acquiring an orange colour on being mixed with sulphuric acid, and a green colour by being boiled with hy-

drochloric acid and alcohol. (See page 114.) *Oxalic acid*.—If the substance contains oxalic acid, its neutral solution produces an immediate precipitate in a solution of sulphate of lime, insoluble in acetic acid, but soluble in hydrochloric acid. (See page 126.) This precipitate of oxalate of lime is distinguished, and may be separated from, tartrate of lime by its insolubility in a cold solution of caustic potash, in which tartrate of lime is soluble. Other tests for *tartaric acid* have just been noticed. *Bromic acid*, *phosphorous acid*, *selenic acid*, and *selenious acid* are best recognised by the application of tests above mentioned to separate portions of the original substance.

The solution filtered from the precipitate produced by nitrate of barytes may contain, besides the acids noticed in the Table at page 193., acetic acid, hydrobromic acid (a bromide), hypermanganic acid, manganic acid, hyposulphurous acid, hyposulphuric acid, nitrous acid, and hydrocyanic acid (a cyanide).

The course to be pursued for the detection of hydrochloric acid, hydriodic acid, nitric acid, and chloric acid, is the same as that already prescribed. *Acetic acid* is discovered by distillation with sulphuric acid and digestion of the product with excess of protoxide of lead. (See page 138.) (For the characters by which *hydrobromic acid* (or a bromide) is detected, see page 145.) Soluble *hypermanganates* and *manganates* are sufficiently characterised by their colour, and by the ease with which they are decomposed by most acids and all deoxidizing agents. (Pages 116, 117.) *Hyposulphites* and *hyposulphates* are decomposed when mixed with strong sulphuric acid, with liberation of sulphurous acid, which is readily detected by its odour. In this decomposition, hyposulphites afford free sulphur, but hyposulphates do not. (See pages 151, 153.) *Nitrites* are recognised by their property of disengaging, when mixed with an acid, nitric oxide gas, which forms ruddy fumes of nitrous acid by uniting with the oxygen of the air. (For the mode of detecting *hydrocyanic acid*, or a soluble cyanide, see page 123.)

2. *The substance is insoluble in water*.—If the substance is insoluble in water, but soluble in acids, it may be submitted to the course of operations directed at page 197. for the detection of the acids included in the list at page 167. ; and for the detection of those mentioned at page 208., separate portions of the substance may be examined for individual acids by the tests just mentioned. Another mode of procedure, in such a case, is to digest the substance for a long time in a boiling solution of carbonate of soda, to neutralize the filtered liquid with acetic acid, and examine the solution for the various acids, as that of a substance soluble in water. If the only bases

present in the substance are metals proper, or their oxides, the substance may be mixed with water, and treated with sulphuretted hydrogen or hydrosulphate of ammonia, according to the nature of the bases present; after filtering the liquid from the metallic sulphuret thus formed, it may be examined for acids, as the solution of a substance soluble in water. The manner of detecting the presence of phosphoric acid in phosphate of iron (described at page 128.) is an example of the latter mode of determining the acid of an insoluble substance. Cyanides of metals proper, not decomposable by dilute acids, are best detected by such a process. (page 143.)

If the insoluble substance is not decomposed by a boiling solution of carbonate of soda, it should be fused with carbonate of soda, as described at page 199., and the aqueous solution of the fused mass be treated as already described. Decomposition with carbonate of soda in the humid way, however, should be first attempted, as several of the acids considered in the present chapter suffer decomposition when their compounds with bases are strongly heated.

CHAPTER IV.

EXAMPLES OF THE QUALITATIVE ANALYSIS OF METALLIC ALLOYS.

THE following illustrations of the qualitative analysis of *German silver* and *Newton's fusible metal*, conducted according to the course prescribed in the second chapter of the present division of this work, may prove useful to the student. In the first example, positive indications are given of the existence of copper, nickel, and zinc in the alloy; but the tests for all other metals afford negative results. In the second example, nothing is detected except tin, bismuth, and lead.

1. *Qualitative analysis of German Silver.*

Dissolve the metal in nitric acid, evaporate off the excess of acid, add a little hydrochloric acid, and dilute the mixture with water. (Hydrochloric acid produces no precipitate of silver, therefore that metal is absent.) Transmit sulphuretted hydrogen gas through the solution to saturation, then filter the liquid, and wash the black precipitate thereby produced with water.

a. Examination of the precipitate formed by sulphuretted hydrogen. — After being washed, the precipitate is digested in hot hydrosulphate of ammonia. The precipitate neither entirely nor partially dissolves, for a few drops of the liquid leave no fixed residue when evaporated to dryness. A black sulphuret remains undissolved, which dissolves in strong nitric acid (hence no mercury is present); the concentrated solution affords no precipitate on being largely diluted (therefore, bismuth is absent); and it gives no precipitate with sulphuric acid (therefore lead is absent). Ammonia added in excess produces an intense blue liquid (hence *copper* is present).

b. Examination of the liquid filtered from the precipitate produced by sulphuretted hydrogen. — Add to it, first, ammonia, and then an excess of hydrosulphate of ammonia. A blackish precipitate is produced, which

is collected on a filter, washed, and dissolved in aqua regia. To this solution ammonia is added in excess.

| | |
|---|---|
| Traces only of peroxide of iron are precipitated. | In the liquid filtered from the slight precipitate of peroxide of iron, hydrosulphate of ammonia produces a black precipitate, which is washed and dissolved in aqua regia, and the solution mixed with excess of caustic potash. |
|---|---|

A green precipitate is produced, which, after being washed, is soluble in a mixture of ammonia and carbonate of ammonia: therefore manganese is absent, and either nickel or cobalt present. On testing the ammoniacal liquid for these metals as directed p. 189., the absence of cobalt, and the presence of *nickel*, are proved. Sulphuretted hydrogen produces in the alkaline liquid a white precipitate of sulphuret of *zinc*.

Therefore the constituents of German silver are copper, nickel, and zinc, with traces of iron.

2. *Qualitative analysis of Newton's fusible metal.*—Dissolve the alloy in dilute aqua regia, with the aid of a gentle heat. If a white powder is formed, insoluble in acids, this may be separated and examined before the blowpipe for tin, as described below. Evaporate off most of the excess of acid, dilute, and through the filtered solution pass sulphuretted hydrogen gas: filter the liquid from the precipitate then produced.

The filtered liquid leaves no residue on evaporation: therefore no metal of Class II. or III. (page 167.) is present.

The precipitate produced by sulphuretted hydrogen is treated with ammonia and hydrosulphate of ammonia.

Wash the insoluble portion, and digest it in strong nitric acid. No black sulphuret remains undissolved; hence mercury is absent. The excess of acid being evaporated from the solution in nitric acid, on pouring the liquid into water, a white precipitate appears, arising from the presence of *bismuth*. Filter, and add to the liquid a solution of sulphate of soda: a white precipitate appears, which is sulphate of *lead*.

The liquid filtered from the undissolved sulphuret affords, when neutralized with acetic acid, a precipitate which does not volatilize entirely when strongly heated; hence it contains something besides sulphur. When boiled in strong hydrochloric acid, as described at page 187., it partly dissolves, and the solution yields, on being digested with metallic zinc, a black powder, which becomes converted into a white oxide on being boiled with strong nitric acid. This white oxide, when heated with carbonate of soda on charcoal before the blowpipe, gives a button of metallic *tin*, recognised by its fusibility and malleability. The tests for the other metals whose sulphurets are soluble in hydrosulphate of ammonia afford negative results.

The constituents of Newton's fusible metal, therefore, are bismuth, lead, and tin.

CHAPTER V.

QUALITATIVE ANALYSIS OF SILICATES.

Means of effecting solution.—THE first operation consists in the reduction of the mineral to an impalpable powder, its perfect solution depending greatly on the minuteness of its division. It is first crushed between folds of paper in a vice, or on an anvil with a hammer; or if the mineral is too hard for this, in a steel diamond mortar, the powder being in this case digested in dilute hydrochloric acid* to remove any portions of iron it may have acquired from the mortar. Its pulverization is completed in an agate mortar, and, if necessary, by levigation, affusion of water, and decantation. When the mineral is extremely hard, it is apt, during pulverization, to scratch the mortar, and thus acquire some portions of agate which have been rubbed off.

A portion of the powdered mineral is next treated with concentrated hydrochloric acid, in a porcelain bason, with the application of a gentle heat. Some silicates are immediately acted on by the acid; others, only by a very long digestion; and some, in fact the greater number, in no degree whatever.

If fully decomposed by hydrochloric acid, all the bases formerly united to silica have become chlorides, and are dissolved on the addition of a little water; while the silica remains in the free state, generally in the form of a light flocculent jelly. If any gritty particles are perceived on stirring with a glass rod against the bottom of the bason, the mineral is not entirely decomposed.

Silicates which resist the action of hydrochloric acid may be rendered soluble in it by first fusing them (in the most minute state of division) with three or four times their

* The harder silicates are not acted on by hydrochloric acid.

weight of carbonate of potash or soda; a silicate of the alkali is then formed, carbonic acid gas being at the same time evolved. The two powders may be mixed in the platinum crucible in which the fusion is to be performed, by means of a glass rod; the crucible is covered, brought gradually to a heat sufficiently high to fuse the mass, and sustained at this temperature for half an hour. The fused mass is then moistened with water, removed from the crucible into a porcelain bason, and treated with pure hydrochloric acid. Effervescence of carbonic acid now occurs; the bases formerly united to silica dissolve in the acid, becoming chlorides, and silica remains in the state of an insoluble jelly. Other substances than silicates, naturally insoluble in acids, are rendered soluble by similar treatment.

To avoid loss of solutions by effervescence, it is necessary, in quantitative analyses, to place the capsule containing the solution within a larger one, to retain the projected drops, which must afterwards be washed into the solution; or a funnel, whose diameter at top is a little less than that of the bason, may be inverted within it, so that the drops spirted within the funnel shall fall again into the bason.

There are a few silicates which resist the action of even carbonates of soda and potash: to effect the decomposition of these, caustic potash, to the amount of about four or five times the weight of the mineral, is employed, instead of the alkaline carbonate, and the heating then performed in a silver instead of a platinum crucible, heated carefully over the spirit lamp with a circular wick. The crucible must be well closed with its lid, as the escape of water from the hydrate of potash produces violent ebullition, which might cause a serious loss in quantitative analyses. A mixture of one part of hydrate of potash and three of carbonate of soda is found convenient for this operation, as the fusion may then be performed in a platinum crucible.

When the mineral is to be examined for alkalies, it is obvious that neither carbonate of potash nor of soda can be used: instead of these, if insoluble in hydrochloric acid, having made a previous investigation of the other consti-

tuents by the ordinary methods, the mineral is decomposed by being heated with carbonate of barytes, or, what is preferable, with quick-lime; the last, however, requires a very intense heat. The solution in hydrochloric acid is made in the same manner as if an alkaline carbonate had been employed: barytes is separated from the solution by sulphuric acid; or if lime is used, that earth is removed by a solution of carbonate of ammonia. (See the description of such a process as this, for the quantitative estimation of the alkalis in silicates undecomposable by acids.)

The ordinary constituents of silicates are, silicic acid, alumina, magnesia, lime, protoxide of iron, oxide of manganese, potash, and soda. The following Tables contain directions for the detection of each of these; but it rarely happens that more than three or four bases exist in the same mineral.

The only known natural silicates which contain other ingredients, as essential constituents, than those which may be discriminated by the Tables, are the following:—

| Names of the particular Constituents. | Names of the Minerals. |
|--|--|
| Barytes - - - | Barytes-harmotome; brewsterite. |
| Boracic acid - - | { Axinite; botryolite; datholite; tourmaline; mica; lepidolite; pinite. |
| Carbon - - - | { Pyrrorthite. (Many minerals contain a little organic matter.) |
| Cerium, oxide of - | { Cerite; cerine; gadolinite; orthite; pyrror- thite. |
| Chlorine - - - | Sodalite; eudialite; pyrosmalite. |
| Chromium, oxide of - | { Several minerals having a green colour, as emerald, serpentine, &c.; pyrope. |
| Copper, oxide of - | { Diopase; chrysocolla; cyprine; cerine; allo- phane. |
| Fluorine - - - | { Apophyllite; chondrodite; chabasite; horn- blende; mica; carpholite; scapolite; topaz. |
| Glucina - - - | { Cymophane; euclase; gadolinite; helvine; beryl. |
| Lead, oxide of - | Thorite; siliceous oxide of zinc. |

| Names of the particular Constituents. | Names of the Minerals. |
|--|---|
| Nickel, oxide of - | Chrysoprase ; pimelite ; olivine. |
| Phosphoric acid - | Lepodilite ; sordawalite. |
| Strontian - - | Brewsterite. |
| Sulphur - - | Helvine ; haüyne ; spinellane ; lapis-lazuli. |
| Tantallic acid - | Traces in emerald. |
| Thorina - - | Thorite. |
| Tin, oxide of - | { Traces in emerald ; euclase ; siliceous oxide of zinc ; thorite ; olivine. |
| Uranium, oxide of - | Pitchblende ; thorite. |
| Yttria - - | Gadolinite ; orthite ; pyrrorthite. |
| Zinc, oxide of - | Siliceous oxide of zinc. |
| Zirconia - - | Zircon ; eudialite |

Qualitative Analysis of Silicates.

The solution is made either in hydrochloric acid, or by fusion with an alkali and subsequent solution in hydrochloric acid. If protoxide evaporate the solution to dryness, and treat the dry mass with dilute hydrochloric acid; the residue undissolved is *silicic acid*. If protoxide of iron is present (ascertained by red prussiate of potash), peroxidize it by heating the solution with a few drops of nitric acid. To the solution add muriate of ammonia and excess of caustic ammonia.

The precipitate may contain alumina and peroxide of iron: filter, wash, and redissolve it in a little hydrochloric acid, add to the solution an excess of potash, and boil the mixture.

Oxide of iron remains undissolved by potash. Confirm this indication by the application, first, of acetic acid in excess, and then of yellow prussiate of potash.

The filtered solution may contain magnesia, oxide of manganese, lime, potash, and soda: evaporate off most of the excess of ammonia, add oxalate of ammonia, boil and filter.

The precipitate is oxalate of lime. It may also contain a trace of oxalate of manganese.

To the filtered solution add hydrosulphate of ammonia.

The precipitate is sulphuret of manganese. Confirm this result by the blowpipe test for manganese.

Decompose the excess of hydrosulph. ammonia by evaporation and addition of hydrochloric acid. To a portion of the solution add ammonia (if acid) and phosphate of soda. If a white precipitate is formed on agitation, this is phosphate of magnesia and ammonia. If no magnesia is present, and no fixed alkali has been added, evaporate the other portion of the solution to dryness, and ignite the residue. Examine this residue by the tests for *potash* and *soda* (p. 191.). If magnesia is present, and no fixed alkali has been added, after precipitation by hydrosulphate of ammonia and filtration, evaporate the solution to dryness, ignite the residue, and redissolve it in water. The solution may contain chloride of potassium, chloride of sodium, and chloride of magnesium. Add to it a strong solution of caustic barytes.

Magnesia is precipitated.

Add sulphuric acid to the solution.

Sulphate of barytes is precipitated. Evaporate the solution to dryness, ignite the residue, and redissolve it in water. Examine the solution for *potash* and *soda* (p. 191.).

Analysis of a Silicate insoluble in Hydrochloric Acid, suspected to contain an Alkali.

Calcine the mineral with five or six times its weight of carbonate of barytes, and treat the ignited mass with hydrochloric acid. Silica remains undissolved. To the solution in hydrochloric acid add carbonate of ammonia and hydrosulphate of ammonia : boil the mixture, and pour it upon a filter.

The precipitate may contain carbonate of barytes, carbonate of lime, alumina, sulphuret of manganese, and sulphuret of iron.

The solution may contain magnesia, alkali, traces of lime, and barytes. Add to it a solution of oxalate of ammonia, and filter the mixture.

Lime and barytes are precipitated.

Evaporate the filtered solution to dryness, ignite the residue, redissolve it in water, and add a strong solution of caustic barytes.

Magnesia is precipitated.

The solution contains alkali and barytes. Add dilute sulphuric acid.

Sulphate of barytes is precipitated.

Evaporate the filtered solution to dryness, ignite, and redissolve the residue in water. Examine the solution for *potash* and *soda*. (See page 191.)

EXAMPLES OF THE QUALITATIVE ANALYSIS OF SILICATES.

1. STILBITE.

Dissolve the powdered mineral in hydrochloric acid ; evaporate the solution to dryness, and treat the residue with dilute hydrochloric acid.

The insoluble residue is *silica*. (Red prussiate of potash gives no blue precipitate ; therefore no nitric acid need be applied to peroxidize iron.) Add excess of caustic ammonia. (As free hydrochloric acid is present, the addition of muriate of ammonia is unnecessary.)

A white precipitate falls, which is entirely soluble in potash ; hence *alumina* is present.

Add oxalate of ammonia to the filtered solution.

Oxalate of *lime* is precipitated.

A drop of the solution evaporated to dryness on platinum foil leaves no fixed residue after ignition.

The constituents of stilbite are, therefore, silica, alumina, and lime.

2. HORNBLLENDE.

Fuse the mineral with carbonate of soda, dissolve the fused mass in hydrochloric acid, and separate *silica* by evaporation and re-solution of the residue. After a little nitric acid has been applied to peroxidize iron, add, first muriate of ammonia (unless the solution is very acid), and then caustic ammonia.

The precipitate is filtered and dissolved in hydrochloric acid. To the acid solution add excess of potash, and boil the mixture.

Add oxalate of ammonia to the filtered solution.

Peroxide of *iron* remains undissolved.

Muriate of ammonia, added to the alkaline solution, produces a precipitate of *alumina*.

Oxalate of *lime* is precipitated.

Phosphate of soda gives a white precipitate of phosphate of *magnesia* and ammonia in the liquid filtered from the oxalate of lime.

Hornblende therefore contains, silica, alumina, oxide of iron, lime, and magnesia.

3. LEPIDOLITE.

(1.) Dissolve the mineral in hydrochloric acid, after fusion with carbonate of soda. *Silica* is separated in the usual manner.

Add muriate of ammonia and caustic ammonia to the solution.

A white precipitate is formed, almost wholly soluble in potash; hence *alumina* is present. (Sometimes a trace of oxide of manganese remains.)

Oxalate of ammonia produces no precipitate in the filtered solution; hence lime is absent. Hydrosulphate of ammonia gives a flesh-colour precipitate of sulphuret of *manganese*.

(2.) Examine for alkalis by fusion with carbonate of barytes.

To the solution in hydrochloric acid separated from silica add carbonate of ammonia and hydrosulphate of ammonia.

The precipitate contains carbonate of barytes, carbonate of lime, alumina, and sulphuret of manganese: filter.

Add a solution of oxalate of ammonia to the filtered solution.

Traces of barytes and lime are precipitated.

The solution leaves a residue on evaporation and ignition. Tartaric acid and chloride of platinum indicate the presence of *potash*. Phosphate of soda and ammonia gives a white precipitate, on long standing, of phosphate of *lithia* and soda. *Lithia* is also discoverable by the blowpipe.

Lepidolite therefore contains, silica, alumina, manganese, potash, and lithia.

CHAPTER VI.

QUALITATIVE ANALYSIS OF MINERAL WATERS.*

THE first point to be determined in the qualitative examination of a mineral water is, to which of the five principal classes of waters does the one in question belong?

1. *Carbonated*, — containing free carbonic acid.
2. *Sulphureous*, — containing sulphuretted hydrogen.
3. *Chalybeate*, — containing carbonate of iron.
4. *Alkaline*, — containing bicarbonate of soda.
5. *Saline*, — containing much neutral salts.

1. If the water reddens blue litmus paper before being boiled, but not afterwards, and the blue colour of the reddened paper is restored on warming it, it is carbonated.

2. If it possesses a nauseous odour, and gives a black precipitate with acetate of lead, it is sulphureous.

3. If after the addition of a few drops of hydrochloric acid it gives a blue precipitate with yellow or red prussiate of potash, the water is a chalybeate.

4. If it restores the blue colour to reddened litmus paper, after being boiled, it is alkaline.

5. If it possesses neither of the above properties in a marked degree, and leaves a large residue on evaporation, it is a saline water.

The substances which commonly enter into the composition of a mineral water are, —

Acids. — Sulphuric, carbonic, phosphoric, silicic, and hydrochloric (chlorides).

Bases. — Potash, soda, lime, oxide of iron, magnesia, and alumina.

* If practicable, the water should always be collected near the mouth of the spring, and secured in well-closed vessels.

Besides these, other constituents are sometimes found, but they are comparatively of much rarer occurrence : these are, —

Acids. — Nitric, sulphurous, boracic, and some organic acids produced by the decomposition of vegetable matter (crenic, apocrenic, and puteanic).

Bases. — Lithia, strontian, oxide of manganese, oxide of zinc, and oxide of copper.

To determine with accuracy all the ingredients which may exist, the water should be concentrated by evaporation nearly to dryness, although a cursory examination, sufficient for many purposes, may be performed on the water in its ordinary state. On boiling, most waters evolve a gas, which in carbonated, alkaline, and chalybeate waters is chiefly carbonic acid ; and in sulphureous, sulphuretted hydrogen : all waters which are exposed to the atmosphere at ordinary temperatures contain also oxygen and nitrogen, though not in the proportions in which these gases exist in the atmosphere. In an extended examination the liberated gas must be collected in the mercurial trough.*

While the gas is evolved by ebullition, a precipitate is formed in chalybeate, carbonated, and most saline waters, which may contain silica, carbonates of lime, magnesia, and strontian, peroxide of iron, fluoride of calcium, and phosphate of alumina. As this precipitate is to be collected and analyzed, particular attention must be paid to the perfect filtration of the water before evaporation, that no solid matter diffused through the water may contaminate the precipitate actually deposited from a state of solution.

When the water is evaporated to dryness, and the residue treated with distilled water, the precipitate formed during ebullition remains undissolved, while all the soluble matters dissolve, forming a solution which may contain potassium, sodium, calcium, and magnesium, combined with chlorine, iodine, and bromine, or as nitrates or sulphates of the oxides of these metals.

* For the means of collecting the gas, see the "Quantitative Analysis of Mineral Waters."

By evaporating the water to dryness, and treating the residue with water, three classes of constituents, therefore, are separated, each of which is to be examined independently: this is the first step in the analysis. 1st. The gases held in solution in the water in its natural state; 2d, the bodies held in solution by the gas, and rendered insoluble by evaporation; and 3d, bodies which are permanently soluble, and therefore redissolved when the dry residue is treated with pure water. The qualitative analysis of each class is conducted in the following manner: —

I. FOR THE GASES EVOLVED.

Into the gas contained in a jar over mercury introduce a little solution of potash free from carbonate.

Absorbed—carbonic acid and sulphuretted hydrogen. Test the original water with lime-water for *carbonic acid*, and with acetate of lead for *sulphuretted hydrogen*. (pp. 123. 150.)

Not absorbed by potash — oxygen and nitrogen: introduce a stick of phosphorus.

Oxygen is absorbed.

Nitrogen remains.

II. FOR THE BODIES RENDERED INSOLUBLE BY EVAPORATION.

Treat the matter with pure hydrochloric acid, and evaporate the solution to dryness. Reserve a small portion of the residue to test for *fluorine*, by heating it with sulphuric acid in contact with glass (see page 124.), and treat the remainder with dilute hydrochloric acid. The insoluble residue is *silica*. The examination of the solution filtered from the silica is conducted according to the following Table.

Examination of the Solution in Hydrochloric Acid of the Precipitate formed on Ebullition.

The second solution in hydrochloric acid may contain lime, magnesia, strontian, lithia, phosphate of alumina, oxide of iron (potash and soda).
(Liebig; *Handwörterbuch*.)

Add excess of ammonia to the solution, and filter.

The precipitate may contain oxide of iron, phosphate of alumina, and traces of magnesia and manganese. Filter, and dissolve it in hydrochloric acid; add excess of potash to the solution, and boil the mixture.

The precipitate contains oxide of iron, traces of manganese, phosphoric acid, and magnesia. Treat it with muriate of ammonia, and add hydrosulphate of ammonia.

The precipitate consists of sulphuret of iron, with a trace of manganese.

The solution contains alumina with phosphoric acid. Saturated with an acid, and then add excess of ammonia. Alumina or phosphate of alumina, is precipitated.

To the solution, which may contain lime, magnesia, strontian, lithia, and manganese, add hydrosulphate of ammonia.

Sulphuret of manganese is precipitated. Saturate the solution with a free acid, and boil; add oxalate of ammonia.

The precipitate contains oxalate of lime and oxalate of strontian; convert these bodies into dry and neutral nitrates (by calcination and digestion of the carbonates thus formed in nitric acid), and treat the nitrates with alcohol.

The insoluble residue is nitrated of strontian.

The solution contains nitrate of lime.

The solution contains magnesia, lithia, (soda, potash); evaporate to dryness, calcine the residue, and dissolve it in water.

The insoluble residue, together with the precipitate produced in the solution by sulphuret of barium, contains all the magnesia. This earth is separated from barytes by sulphuric acid.

To the solution add sulphuret of barium, and filter; add sulphuric acid to the filtered liquid, again filter, evaporate, and calcine the dry mass. The residue consists of sulphates of the alkalies.

III. EXAMINATION OF THE BASES IN THE SOLUTION FILTERED FROM THE PRECIPITATE PRODUCED BY EBULLITION.

This may contain lime, magnesia, potash, soda, and lithia.

If lime is present, oxalate of ammonia gives a white precipitate of oxalate of *lime*. Filter the solution from the precipitated oxalate, and add phosphate of ammonia and a little free ammonia to test for magnesia, which should produce a white precipitate of phosphate of *magnesia* and ammonia, if magnesia is present.

To another portion of the water add a solution of caustic barytes.

| | | |
|---|--|--|
| The precipitate contains magnesia, lime, and sulphate of barytes. | The filtered solution contains lime, barytes, and alkalis: add carbonate of ammonia to it. | |
| | The precipitate is carbonate of lime and carbonate of barytes. | The solution contains ammoniacal salts, <i>potash</i> , <i>soda</i> , and <i>lithia</i> . Evaporate to dryness, and calcine the dry mass to expel ammoniacal salts; the residue consists of alkaline chlorides. Dissolve it in water, and test the solution with chloride of platinum, tartaric acid, and antimoniate of potash, and examine a portion of the dry salts by the blowpipe. |

To discover *lithia*, a large quantity of the water should be evaporated to dryness, the residue dissolved in a small quantity of water, and filtered to separate the insoluble portion. To the solution, phosphate and carbonate of soda are added, the mixture is evaporated to dryness, and the residue treated with water, when, if lithia is present, this alkali remains undissolved, in the state of phosphate of lithia and soda.

IV. EXAMINATION FOR ACIDS.

First Portion. *Carbonic acid* and *sulphuretted hydrogen*.

—If the water, fresh from its source, feebly reddens blue litmus paper, and the colour of the paper is restored on gently heating it, this indicates the presence of *carbonic acid*. Lime-water then occasions a precipitation of carbonate of lime.

Carbonic acid may exist in three different states in mineral waters. 1st, as the free uncombined acid dissolved in the water; 2d, holding in solution earthy carbonates; and 3d, combined with potash or soda as bicarbonates. These different states may be distinguished by the following characters: — 1st. If the precipitate of carbonate of lime produced in the water by the addition of a small quantity of lime-water is redissolved by an excess of the mineral water, it contains the uncombined acid. 2d. If, on the contrary, the precipitated carbonate of lime does not dissolve in any excess of the water, and during ebullition a precipitate is formed which effervesces with acids, the carbonic acid is combined with earthy carbonates. 3d. If no precipitate is formed while the gas is evolved by ebullition, and the solution becomes strongly alkaline, effervescing with acids, alkaline bicarbonates existed in the original water.

Sulphuretted hydrogen is detected by the black precipitate produced by salts of lead or copper, and by the nauseous odour possessed by the water. If, after boiling for a considerable period, a black precipitate is still produced by the metallic solutions, *alkaline sulphurets* are contained in the water.

Second Portion. For *sulphuric* and *hydrochloric acids*. —

Hydrochloric acid is shown by the white curdy precipitate produced by nitrate of silver, insoluble in nitric acid, but soluble in ammonia. (page 141.) To the solution filtered from chloride of silver add a solution of nitrate of barytes and a little nitric acid; a white precipitate indicates *sulphuric* acid. (page 132.)

Third Portion. *Iodine* and *bromine*. — Evaporate a large quantity of the water to a very small bulk, and divide the residue into two portions. With one mix a little starch, and allow chlorine gas to fall on the surface of the liquid from a bottle of chlorine water. If a trace of *iodine* exists, it will be immediately recognised by the blue colour produced. (page 148.)

To discover *bromine*, add a little chlorine water to the other portion: if this element is present, a brown colour is developed,

which is removed by agitation with ether. On standing for some time, the ether rises to the top, carrying with it all the bromine; add potash to the ethereal solution, evaporate to dryness, redissolve in water, and apply other tests for bromine. (page 145.)

Fourth Portion. For *nitric* and *boracic acids*. — Evaporate to dryness. If *nitric acid* is present, the dry salt deflagrates when heated strongly and touched with a glowing match. (page 154.)

When the dry residue is moistened with alcohol and a little sulphuric acid, if the alcohol burns with a green flame, *boracic acid* is present. (page 122.)

Fifth Portion. For *sulphurous acid*. — This acid is recognised by the action of iodic acid. (page 133.) Strong sulphuric acid causes an effervescence of sulphurous acid gas from a concentrated solution.

Sixth Portion. For *phosphoric acid*. — Sulphate of magnesia mixed with a little free ammonia causes a white crystalline precipitate of phosphate of magnesia and ammonia. (page 127.)

Seventh Portion. For *organic acids* (crenic, apocrenic, and puteanic). — The dry residue of evaporation becomes carbonized when heated to redness, if it contains organic bodies.

To the preceding extended examination I subjoin a plan of a simpler and more cursory one, which will, in many cases, afford sufficient information on the nature of the water.

Different quantities of water are to be used for each test.

1. Oxalate of ammonia or binoxalate of potash is applied as a test for the presence of *lime*. (page 53.)

2. Phosphate of soda with some free ammonia, is next applied as a test for *magnesia*. (page 54.)

If oxalate of ammonia and phosphate of soda with ammonia give precipitates before (but not after) ebullition, the lime and magnesia exist entirely as carbonates.

3. Yellow or red prussiate of potash gives a blue precipitate if *iron* is present. If the water is carbonated, and

has been boiled, a few drops of hydrochloric acid should be added to redissolve the precipitate formed on ebullition.

4. Tincture of nut-galls, with a few drops of lime-water, gives a blackish brown colour, when a very minute quantity of *iron* exists in the water. If this tincture and prussiate of potash give indications of iron after boiling for half an hour, when no acid has been added, the iron does not exist solely in the state of carbonate.

For *carbonic acid* apply the tests of litmus and of lime-water; for *sulphuretted hydrogen*, that of acetate of lead; for *sulphuric acid*, that of chloride of barium; and for *hydrochloric acid*, that of nitrate of silver.

These directions for the qualitative analysis of mineral waters do not, however, indicate the actual salts which are present as they exist, but only their respective acids and bases. The arrangement of these in the water can seldom be determined by any process of qualitative analysis, except by the application of a rule, which is not without exceptions, that the strongest acids are in combination with the strongest bases. But when the quantitative analysis of the water has been performed, the arrangement of the acids and bases can generally be ascertained with tolerable accuracy, from the difference which exists in the combining numbers of bodies. Thus, the quantities of sulphuric acid required for neutralization by the two bases, magnesia and potash, differ considerably; so that an amount of sulphuric acid having been found which is equivalent to the magnesia, and not to the potash, the former, and not the latter, is concluded to be in the state of sulphate. Another acid will probably be found whose amount will correspond to that of the potash, with which therefore the alkali was probably united.

CHAPTER VII.

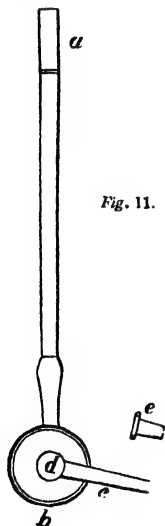
ON THE USE OF THE MOUTH BLOWPIPE IN QUALITATIVE ANALYSIS.*

SECTION I.

BLOWPIPE MANIPULATIONS, AND GENERAL REMARKS ON BLOWPIPE ANALYSIS.

FROM its ready application, manageability, and general convenience, and from the highly characteristic results obtained by it with several chemical substances, the blowpipe is of great value to the chemist, as a means of confirming results previously obtained or afterwards to be sought in humid analysis. By its means, the temperature of a small quantity of a substance can be raised almost instantaneously to a white heat. Now when this is done in different ways, as in a closed tube, in an open tube, alone or mixed with other bodies, or in different parts of the flame, positive conclusions are attained respecting the nature of the bodies operated on.

This little instrument is simply a tube open at both extremities, the aperture in one being contracted so as to become capillary, through which a small stream of air is forced upon a flame. It would be out of place here to enter into details respecting the construction of the various kinds of blowpipes. A very convenient one is Voigt's,



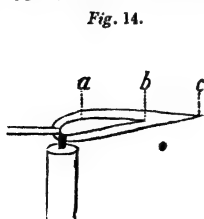
* For more minute instructions in blowpipe analysis, the reader is referred to an excellent treatise on that subject by Professor Plattner, of which an English translation by Dr. Muspratt has recently appeared.

which is represented in the preceding cut (*fig. 11.*). It consists of a brass tube, with an ivory mouth-piece *a*, at one extremity, and at the other a circular box *b*, from which issues the small tube *c*, moveable round the centre *d*, by which any degree of obliquity may be given to the flame: *e* is a brass or platinum jet, which fits on the tube *c*. The only inconvenience attending this form is, that the tube *c* becomes loose by long usage. Griffin's (*fig. 12.*), which is of the same construction as Black's, is a cheaper and equally efficient instrument.

It is made of japanned tin, with a brass nozzle.

As the current of air which is supplied ought to be continuous, its production requires some attention and address. The air is not blown directly from the lungs, but is forced from the mouth by means of the cheeks. The difficulty consists in inspiring and expiring through the nose, while a continued stream escapes from the mouth. This may be attained by attention to the following directions:—Inflate the mouth fully, and then, with the lips firmly closed, and the back of the mouth closed by the tongue, breathe freely through the nostrils. While the respiration proceeds, and the mouth is inflated, allow a little air to escape through a very minute opening between the lips, renewing the supply in the mouth by occasionally admitting air from the lungs without interfering with the process of respiration through the nose. A little practice renders the operation easy.

The effect of this current of air through a flame is to cause a double combustion: the interior, which before could not burn for want of air, now burns by means of the air forced through the blowpipe; the external atmosphere supplying air for the combustion of the exterior of the flame as before. This will be more apparent by reference to the annexed figures. *Fig. 13.*



represents a section of the ordinary flame of a candle: the interior cone (*ab*) is composed of combustible vapours or gases formed from the tallow, prevented from burning by having no access to the air, combustion taking place only on the exterior *b*, where the vapour is in contact with the atmosphere. Let air be admitted into the interior, as is done by the blowpipe, and these gases and vapours are burned, as they are on the exterior: the flame has then the appearance of *fig. 14.*, *a* representing the interior portion of the flame where combustion takes place. Between the points *b* and *c* inflammable gases, still unburned, exist. Now this portion of the flame possesses properties very different to those possessed by the portions either beyond or within it. If oxide of copper is heated in this portion, oxygen is abstracted from the oxide by the combustible gases (which at this high temperature exhibit an intense affinity for oxygen), and metallic copper is produced: on the other hand, if metallic copper is heated beyond the point *c*, it is again oxidated, the oxygen being now supplied from the external atmosphere. From possessing such different properties, these portions of the flame are called the oxidating and the deoxidating flames. The latter is also called the reducing flame. The chief oxidating effect is, however, produced beyond the flame; and this action is greater the farther the substance is from it, provided the temperature be maintained sufficiently high.

The apparatus to be used with the blowpipe can be but briefly described here. For a flame, where coal-gas is available, that is to be preferred: the aperture of the burner is made of an oblong shape, instead of round, the current of air being blown lengthways. A candle having a large wick may also be employed; but it is inconvenient, from the melting of one side, by the bent flame and by the radiant heat of the ignited substance under examination. The blowpipe oil-lamp recommended by Berzelius consists of a tin cylinder, about one inch in diameter, and four inches long, having a flat wick about three quarters of an inch broad. It is supported at one end by a retort-stand.

Various supports are used to hold the substance while

exposed to the blowpipe flame, depending on the object of the operation to which the matter is submitted. When heated alone, a pair of tongs or forceps, having small platinum points, a piece of platinum foil held by forceps, a platinum capsule, or a piece of dense charcoal, may be used. When heated with fluxes, as borax or microcosmic salt, a piece of small platinum wire is usually employed, bent twice at right angles at one extremity, to retain the fused globule: a piece of charcoal or a bone-earth cupel is also employed for this purpose. Glass tubes, open or closed at one end, are used when it is suspected something volatile may be given off. None but hard German glass should be used for blowpipe experiments.

The principal operations to be performed are, —

- 1st, heating the substance in a glass tube sealed at one end;
- 2nd, in a tube open at both ends;
- 3rd, upon charcoal;
- 4th, between the platinum points of a pair of forceps, or upon a piece of platinum foil; and,
- 5th, with fluxes or other reagents.

The chief objects of the *first* operation are, to ascertain whether a sublimate occurs, or whether the substance contains any volatile matters; whether decrepitation takes place; whether the volatile products possess an acid or an alkaline reaction, or are neutral; whether the substance becomes black on being heated, showing the presence of organic matter; and the degree of fusibility of the substance. The tubes employed should be about two or three inches in length, and from one eighth to one fourth of an inch in diameter. The body under examination may occasionally require to be mixed with some reagent, as bisulphate of potash or charcoal.

The *second* operation is done with a view of ascertaining what effect a current of atmospheric air has on the substance at a high temperature; to see if a sublimate is produced; and, if so, whether similar to that in the closed

tube; and whether any peculiar odour is developed. By inclining the tube more or less, we have the means of regulating the current of air which passes: if heated when held nearly horizontal, very little air passes through, but the air increases in proportion as the tube is held more and more vertical. Some substances afford a sublimate in this operation, which do not in the first.

In the *third* operation, that of heating the substance alone, in a small cavity cut in a piece of charcoal, it is to be particularly observed: 1st, whether the substance fuses; 2nd, whether it disengages a peculiar odour (from which the presence of sulphur, arsenic, and selenium is ascertained), both in the exterior and interior flames*; 3rd, whether the substance contains a metallic compound easy of reduction; 4th, whether the charcoal becomes covered with a white or coloured sublimate, indicating the presence of certain volatile metals (as zinc, cadmium, antimony, bismuth, &c.); and, 5th, whether the substance, after strong calcination, affects moistened test-paper, in the manner of alkalies.


In the *fourth* operation, several objects are also to be kept in view. The degree of fusibility of the substance is observed; for which purpose a comparative scale has been established, consisting of the following minerals, in the order of their fusibility, beginning with the least fusible: *sulphuret of antimony, natrolite, garnet, hornblende, felspar, and diallage*. The changes exhibited by the substance must be noticed, as change of colour, intumescence, or deflagration. It must be ascertained whether the substance appears the same in the reducing as in the oxidating flame, and whether any volatile matters are evolved. An important object is to ascertain whether the substance produces any change on the colour of the blowpipe flame. The change, if any, is best seen when the matter just touches the flame at the top, about the middle of its length. In this operation, if the substance is in small

* Sulphur and selenium are best detected in the exterior flame, and arsenic in the interior.

fragments or splinters, it is usually held by a pair of forceps having small platinum points; if in powder, it may be kneaded into a stiff paste, with a little water, and be heated upon a piece of platinum foil.

The *fifth* operation consists in treating the substance with reagents. Except in a few particular cases, the only reagents employed are, borax, microcosmic salt, and carbonate of soda; or a mixture of carbonate of soda with cyanide of potassium.* The object of heating with the first two, is to see whether the substance dissolves; and, if so, what colour glass results both in the interior or reducing, and in the exterior or oxidating,

Fig. 15.

 flame. A platinum wire, bent as in the annexed figure, is generally employed in this operation for borax; but as microcosmic salt gives a very fluid bead when

* *Borax* is fit for use in blowpipe experiments if its solution affords no precipitate with carbonate of soda, nor, after being mixed with nitric acid, with nitrate of barytes or nitrate of silver. If these reagents afford indications of the presence of impurities, the borax is purified by re-crystallization. The water of crystallization is expelled by heating the crystals in a crucible, the temperature not being raised high enough to effect the igneous fusion. The spongy mass thus obtained is preserved for use. It should give a perfectly clear and colourless bead when melted on the platinum wire.

Microcosmic salt, which is the double phosphate of soda and ammonia, is prepared by dissolving together in a small quantity of water 100 parts of crystallized phosphate of soda, and 16 parts of muriate of ammonia: crystals of common salt separate, and the decanted liquid may be evaporated to crystallization. The crystals thus obtained are still further freed from common salt by re-crystallization. When strongly heated, microcosmic salt parts with water of crystallization and with ammonia; the remaining phosphate (metaphosphate) of soda fuses to a clear glass, which possesses a powerful solvent action on most metallic oxides.

The *carbonate of soda* obtained by heating the bicarbonate of soda of commerce to dull redness, for a short time, is fit for use in blowpipe experiments. It should be free from sulphate of soda. Carbonate of soda is used both as a solvent and as a means of assisting the reduction of metallic compounds in the interior blowpipe flame. For the latter purpose, a mixture of equal parts of *carbonate of soda and cyanide of potassium* is in general decidedly superior to carbonate of soda alone. Cyanide of potassium is prepared by heating to redness, in a closed crucible, a mixture of three parts of dry carbonate of potash and eight parts of yellow prussiate of potash, previously rendered quite anhydrous by being moderately heated. This mixture is resolved, at a high temperature, into cyanide of potassium, cyanate of potash, and metallic iron; the two former, being in a fluid state, may be poured out together, upon a clean slab, or into a porcelain basin; the iron remains in a pulverulent state at the bottom of the crucible. The presence of cyanate of potash does not interfere with the applications of cyanide of potassium in blowpipe analyses.

heated, a few additional bends must be made when this salt is used, to prevent the melted drop from falling. Instead of the platinum wire, charcoal may be used to support these fluxes. In all cases, a perfectly clear bead must first be obtained of the flux alone: a small particle of the substance is then stuck to the bead by being moistened, and the bead again melted. If the substance dissolves without communicating any colour to the bead, the effect of adding another small particle should be observed. If the bead is of so dark a colour as to appear black, it should be drawn out, while soft, to a long thread, in which the colour may be easily discerned.

In fusing a substance with carbonate of soda, the principal objects are, to ascertain whether the substance gives a reduced metal upon charcoal, and whether it is soluble in the fused carbonate, giving a *glass*, or insoluble, giving a *slag*. For the detection of a few substances, the colour of the bead is also to be observed: thus, compounds containing sulphur or sulphuric acid are recognised by affording, with carbonate of soda, in the reducing flame, a bead of a yellow, red, or brown colour; and compounds of manganese, by affording, with the same reagent, in the exterior flame, a bead of a green colour.

A bent platinum wire is sometimes employed as the support for carbonate of soda, the powder being mixed with a little water to form a paste, which is placed with the substance on the end of the wire, and moderately heated until quite dry, when it is strongly heated, first in the exterior, and afterwards (if manganese is not the substance sought) in the interior flame. In applying this test for manganese, a platinum wire is the proper support; but in all cases where a substance is to be exposed to a reducing flame with carbonate of soda, charcoal is by far the best support for the mixture. A dense piece should be selected, and a cavity made in it, from one third to one half of an inch in diameter, bored to about one eighth of an inch in depth. The carbonate of soda, in fine powder, is kneaded into a lump with a little water, mixed with the substance for examination, and placed in the charcoal cavity. The mixture is first dried at a moderate heat, and is then strongly heated for some time, a little within

the point of the reducing flame; or, if the object is merely to ascertain whether the substance dissolves or not in the melted soda, the mixture is heated in the oxidizing flame. To discover whether a reduced metal has been formed by the heating, the bead, when cold, is removed from the charcoal, and powdered with a little water, in an agate mortar. The particles of charcoal and soda are washed away by affusion, while any metallic particles present subside to the bottom, and may be further examined as to colour, malleability, &c.

If the substance under examination is a sulphuret, it should be roasted or oxidized in the exterior flame before being exposed to the interior flame. When, however, a mixture of carbonate of soda and cyanide of potassium is employed, instead of carbonate of soda alone, the roasting or oxidation of sulphurets previous to their reduction is unnecessary, as cyanide of potassium possesses the property of reducing sulphurets as well as oxides. The mixture of carbonate of soda and cyanide of potassium may be heated on a charcoal support, in the same manner as carbonate of soda only.

The other reagents occasionally used in blowpipe analyses are, a solution of nitrate of cobalt, bisulphate of potash, and nitre.

The solution of nitrate of cobalt is used principally for the detection of alumina, magnesia, and oxide of zinc. Alumina, when moistened with the solution of cobalt, and moderately heated in the oxidizing flame, acquires a fine blue colour; magnesia, in the same circumstances, becomes rose-red; and oxide of zinc, bright green. Silica and minerals containing lime or an alkali, when strongly heated with solution of cobalt, also acquire a blue tinge, but which is considerably inferior in intensity to that acquired by alumina. If the mineral to be tested by the solution of cobalt is slightly porous, a splinter of it may be moistened with the solution, and held before the flame between the platinum points of a pair of forceps. If the mineral is not porous, but crystalline, it is reduced to fine powder, kneaded into a paste with water, and heated to redness upon a piece of charcoal.

Fusion of a mineral with bisulphate of potash or nitre,

before the blowpipe, is sometimes practised in order to obtain certain constituents of the mineral in an oxidized and soluble form. The solution of the fused mass in water or an acid is tested for various substances in the humid way. The fusion with either of these reagents may be conducted on a small platinum spoon.

In the Tables which immediately follow, are exhibited the most remarkable of the phenomena which metallic oxides present before the blowpipe; then the characters of some acids (in combination) are described; after which tabular views are given of the successive operations (with their subdivisions) which are to be performed, and appearances to be looked for, in the examination of an unknown substance; when, by following the processes of the latter Tables, a clue to the nature of the substance is obtained, the result should be confirmed by examining whether it possesses all the characters which belong to that substance, as contained in the former Tables.

SECTION II. BEHAVIOUR OF

I. ALKALIES

| | Alone. | Colour of Flame produced by moist soluble Salts. | With Borax. |
|------------|--|--|--|
| Potash. | Fusible. | Faint reddish or violet, if no soda is present. | The red glass of borax and ox- ide of nickel is changed to blue. |
| Soda. | Fusible. | Intense yellow (characteristic). | The red glass of borax and nickel is not changed to blue. |
| Lithia. | Fusible. | Crimson (see page 50.). | |
| Barytes. | Infusible. The hydrate and carbonate are fusible. | Pale apple green. (Only for an instant) | Colourless trans- parent bead ; opaque if satu- rated. |
| Strontian. | Ditto. | Intense crimson (characteristic). | Ditto. |
| Lime. | Infusible, gives a strong light. | Reddish purple. | Ditto. |

SUBSTANCES BEFORE THE BLOWPIPE.

AND EARTHS.

| With Microcosmic Salt. | With Carbonate of Soda on Charcoal. | Colour obtained with Solution of Nitrate of Cobalt (in the oxidizing flame). |
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| | | |
| | | |
| A colourless bead, which becomes opaque when cold, if saturated. | Is dissolved, and is then absorbed by the charcoal. | Brick or yellowish red while hot; colourless when cold. |
| Ditto. | Caustic strontian is not dissolved; but the carbonate is, and is absorbed by the charcoal. | Black or grey. |
| Ditto. | Not dissolved; the soda is absorbed by the charcoal. | Ditto. |

| | Alone. | Colour of Flame produced by moist soluble Salts. | With Borax. |
|------------------------|---|--|--|
| Magnesia. | No change. | | Ditto. |
| Alumina. | Ditto. | | A colourless glass, which remains so when cold. |
| Glucina and Yttria. | Ditto. | | A transparent glass ; which becomes milky by being cool- ed. |
| Zirconia. | Infusible, gives a very powerful light. | | Ditto. |

| With Microcosmic Salt. | With Carbonate of Soda on Charcoal. | Colour obtained with Solution of Nitrate of Cobalt (in the oxidizing Flame). |
|---|--|---|
| Ditto. | No action. | Flesh colour after strong heating (characteristic). |
| A transparent glass ; which becomes slightly opaque if an excess of alumina is added. | An insoluble compound is formed, and the excess of soda is absorbed. | A fine azure (characteristic). The colour is distinct only when cold and in daylight. |
| As with borax. | No action. | Greyish black. |
| Scarcely transparent when cold. | Ditto. | Ditto. |

II. OXIDES OF

| | Alone. | | With Borax on the Platinum Wire. | |
|--------------------------------|--|-----------------|---|---|
| | Oxidating Flame. | Reducing Flame. | Oxidating Flame. | Reducing Flame. |
| Anti- mony, oxide of. | Sublimes, giving a greenish blue flame; is reduced on charcoal in the interior flame. The charcoal acquires a white coating. | | Yellow glass while hot; colourless when cold. | Grey at first, from particles of reduced metal, which are afterwards volatilized. |

Oxides of antimony and tin are often obtained together in the course of pipe test. The substance suspected to contain one or both of these and the mixture is exposed on charcoal to the blowpipe reduction which is deposited on the charcoal, antimony is present. But if the and the reduced metal is found to be malleable when the mass is tin may be inferred.

| | | | |
|--------------------------|---|---|--|
| Bismuth, oxide of. | Fusible; dark brown while hot, yellow when cold on wire. Reduced on charcoal. (See "with Carbonate of Soda.") | A faint yellow glass while hot, which is nearly colourless when cold. | Grey, from particles of reduced metal. |
|--------------------------|---|---|--|

The metal with which bismuth is most liable to be confounded, in by the following differences in their blowpipe characters: the suboxide of antimony is white; oxide of bismuth is deposited farther bismuth communicates no colour to the flame, while oxide of anti-

METALS PROPER.

| With Microcosmic Salt on the Platinum Wire. | | With Carbonate of Soda. |
|--|-----------------|---|
| Oxidating Flame. | Reducing Flame. | |
| A faint yellow glass; which is colourless when cold. | As with borax. | A colourless glass on the wire. Reduction takes place on charcoal. The reduced metal is very fusible and brittle, and disengages a white smoke of oxide when heated in the air. |

qualitative analysis, and are distinguished from each other by a blow-oxides is mixed with cyanide of potassium and carbonate of soda, flame. If metallic globules appear, which disengage a white smoke, whole or portions of the metallic globules remain after long blowing, washed with water in an agate mortar (see page 238.), the presence of

| | |
|----------------|--|
| As with borax. | Reduced on charcoal. The reduced metal is brittle; if heated on charcoal it gives a yellow coating of oxide. |
|----------------|--|

blowpipe experiments, is antimony. These metals are distinguished limite of oxide of bismuth deposited on charcoal is yellowish, that of from the particles of metal than oxide of antimony; and oxide of mony imparts to the flame a greenish blue colour.

| | Alone. | | With Borax on the Platinum Wire. | |
|---|--|---|--|---|
| | Oxidating Flame. | Reducing Flame. | Oxidating Flame. | Reducing Flame. |
| Cadmium, oxide of. | Unchanged on platinum foil. | On charcoal is reduced and volatilized; the charcoal acquiring an orange-red coating, which is best seen when cold. | A yellowish glass nearly colourless when cold. If much ox. cadmium is present, the glass is milky. | On charcoal the ox. cadmium is reduced and volatilized; the charcoal acquiring an orange-red coating. |
| Cerium, oxide of. | The peroxide becomes converted into the protoxide in the reducing flame. Unchanged in the oxidating flame. | | A red or orange glass when hot, pale when cold. | Colourless, or nearly so; milk white if saturated. |
| Chromium, oxide of. | No change. | | Yellow or red while hot, green when cold. | Green, both when hot and when cold. |
| When any substance containing oxide of chromium is fused with nitre, forming a yellow solution. (See page 114.) | | | | |
| Cobalt, oxide of. | Not changed. | | A deep blue glass, in both flames, sometimes so dark as to appear black. This test for cobalt is highly characteristic and delicate. | |

| With Microcosmic Salt on the Platinum Wire. | | With Carbonate of Soda. |
|--|-------------------------------|---|
| Oxidating Flame. | Reducing Flame. | |
| A transparent glass, which becomes milky when cooled, if saturated with ox. cadmium. | Reduction takes place slowly. | Not dissolved on plat. wire. On charcoal it is reduced, and cadmium is volatilized. The charcoal acquires a reddish brown coating (characteristic). |
| As with borax. | Colourless. | Not dissolved : the soda is absorbed, and the protoxide remains on the charcoal. |
| Reddish while hot, green when cold, in both flames (characteristic.) | | In oxidating flame on the wire, a dark orange glass when hot, opaque when cold. In reducing flame, opaque, becoming green on cooling. |
| yellow chromate of potash is formed, which dissolves in water, | | |
| As with borax. | | Reduction takes place on charcoal. |

| | Alone. | | With Borax on the Platinum Wire. | |
|----------------------|---|--|--|---|
| | Oxidating Flame. | Reducing Flame. | Oxidating Flame. | Reducing Flame. |
| Copper, oxide of. | The bromide and chloride of copper give a blue flame; most other salts give a green flame. | | A green glass while hot, which becomes blueish on cooling. | A brownish red glass; the colour is increased by the addition of tin. |
| | Fuses. | Reduced, giving a red malleable metal. | | |
| Iron, peroxide of. | Not changed. | Blackens and becomes magnetic. | A yellow or red glass while hot, which becomes pale on being cooled. | A bottle-green glass, which becomes light green on the addition of tin. |
| Lanthanum, oxide of. | Not changed. | | The oxide dissolves, forming a colourless, or very faint rose coloured bead. | |
| Lead, oxide of. | Fuses and gives a clear blue tint to the flame; is reduced on charcoal to a metallic globule, which slowly sublimes, giving a yellow deposit on the charcoal. | | A yellow glass, nearly colourless when cold. | Reduction takes place. |

| With Microcosmic Salt on the Platinum Wire. | | With Carbonate of Soda. |
|---|---|--|
| Oxidating Flame. | Reducing Flame. | |
| As with borax. | A dark green glass while hot, which is opaque and reddish brown when cold. | On the plat. wire, the oxide dissolves, forming a green glass when hot, which is colourless and opaque when cold. Reduction takes place on charcoal, a red malleable metal being formed: the mass should be triturated with water in a mortar (see page 238.). |
| As with borax. | A reddish or greenish glass when hot, which is almost colourless when cold. | Reduced on charcoal, giving a magnetic metallic powder. |
| As with borax. | | Not dissolved: the soda only is absorbed by the charcoal. |
| As with borax. | | A transparent glass on the wire, which is yellow and opaque when cold. Reduction readily takes place on charcoal: the metallic bead is recognised by its colour, softness, and malleability. |

| | Alone. | | With Borax on the Platinum Wire. | |
|-----------------------|-------------------------------------|-----------------|--|---------------------------------------|
| | Oxidating Flame. | Reducing Flame. | Oxidating Flame. | Reducing Flame. |
| Manganese, oxides of. | Infusible. Protoxide becomes brown. | | An amethyst glass, sometimes so dark as to appear black. | The coloured bead becomes colourless. |

Borax, microcosmic salt, and carbonate of soda are both characteristic soda is the best of the three. It is said that when manganese is cannot be detected by borax, but is by caustic soda. (M. Hermann.)

| | | | |
|-------------------|--|--|--|
| Molybdic acid. | It fuses, giving a smoke in the open inclined tube and on the platinum foil. Is reduced with difficulty on charcoal. | A yellowish or reddish glass while hot, which is colourless or opaline when cold. | A brownish red glass on charcoal. |
| Nickel, oxide of. | No change. | Violet when hot, and reddish brown or orange red when cold. | Grey, from reduced metal. |
| Silver, oxide of. | Reduction takes place immediately. | Partly reduced and partly dissolved. The glass is milk-white or opaline when cold. | Grey from reduced metal. The particles of metal slowly aggregate and leave a clear bead. |

| With Microcosmic Salt on the Platinum Wire. | | With Carbonate of Soda. |
|---|-----------------|--|
| Oxidating Flame. | Reducing Flame. | |
| As with borax. But the coloured bead is decolorized in the reducing flame sooner than with borax. | | On the platinum wire, in the outer flame, the green manganate of soda is formed. The action is accelerated by the addition of nitre. |

and delicate tests for the compounds of manganese, but carbonate of accompanied by much of the oxides of cerium and lanthanum, it

| | | |
|---|--|--|
| A colourless or yellowish green glass. | A dark blue or black glass when hot, which becomes green when cold. | Is dissolved on the platinum wire, forming a clear glass, which becomes milk-white on cooling. Reduction takes place on charcoal, a steel grey metallic powder being formed. |
| A reddish glass, which becomes yellow or colourless on cooling. | As in the oxidating flame. The colour disappears on the introduction of tin. | Reduction takes place on charcoal, with formation of metallic nickel, as a white, shining, magnetic powder. |
| A yellowish glass by daylight, which is red by candle-light; opalescent, with ox. silver in excess. | As with borax. | Reduction takes place immediately. |

| | Alone. | | With Borax on the Platinum Wire. | |
|----------------------|---|---|---|--|
| | Oxidating Flame. | Reducing Flame. | Oxidating Flame. | Reducing Flame. |
| Tellurium, oxide of. | Gives the flame a green colour. Fuses and sublimes; is easily reduced on charcoal, with deposition of a white coating of oxide. | | A colourless glass. | A grey glass. |
| Tantalalic acid. | No change. | | A colourless glass, which becomes opaque when heated in an intermittent flame. (The same in both flames.) | |
| Tin, oxides of. | The protoxide becomes peroxide. | Reduction to metallic tin takes place slowly. | A colourless glass, sometimes opaque. | On charcoal, reduction takes place slowly. |
| Titanium, oxide of. | Not changed. | | A colourless glass, which becomes opaque on cooling. | The colour of the glass is first yellow, then amethyst, and becomes darker on cooling. |
| Tungstic acid. | Not changed. | Blackens, but does not fuse. | A colourless or yellow glass, which is clear and colourless or white when cold. | A yellow or orange glass, which becomes darker as it cools. |

| With Microcosmic Salt on the Platinum Wire. | | With Carbonate of Soda. |
|---|---|--|
| Oxidating Flame. | Reducing Flame. | |
| As with borax. | | A clear colourless glass on the wire, which becomes white and opaque on cooling. Reduction takes place on charcoal, with deposition of a white coating of oxide. |
| A colourless glass, which is opaque when cold. (The same in both flames.) | | Combination takes place with effervescence; but without solution or reduction. |
| A colourless glass. | As in the oxidating flame. (No reduction.) | Reduction takes place on charcoal, with formation of a soft and very fusible metal. (See the method of distinguishing between tin and antimony, at page 244.) |
| A yellow or colourless glass while hot, which is colourless when cold. | A yellow glass while hot, which is violet when cold. | The oxide dissolves with effervescence, giving a yellowish glass, which becomes greyish white and opaque on cooling. No reduction takes place on charcoal. |
| A very slightly yellow glass. | A very fine blue glass, which is rendered blood-red by oxide of iron. The blue colour is restored by tin. | On the platinum wire a dark yellow glass is formed, which becomes opaque on cooling. Reduction takes place on charcoal. |

| | Alone. | | With Borax on the Platinum Wire. | |
|--------------------|--|---------------------------------|---|---|
| | Oxidating Flame. | Reducing Flame. | Oxidating Flame. | Reducing Flame. |
| Uranium, oxide of. | The protoxide is converted into the peroxide. | It blackens, but does not fuse. | A yellow glass. | A green glass, which is blackened by an intermitting flame. |
| Vanadic acid. | On charcoal, vanadic acid fuses, and is partially reduced. | | A yellow or colourless glass. | A brown glass when hot, which is green when cold. |
| Zinc, oxide of. | Gives a strong whitish green flame. The oxide is slightly yellow while hot (by daylight), but white when cold. It becomes green when heated with solution of nitrate of cobalt. On charcoal, in the reducing flame, it is slowly reduced, and the charcoal is coated with a white oxide. | | A transparent glass which becomes milky by an intermittent flame. | Reduction takes place on charcoal: the metal volatilizes, and the charcoal is coated with oxide. On the platinum wire the transparent bead becomes white. |

III. BLOWPIPE CHARACTERS OF ACIDS, OR ELECTRO-NEGATIVE BODIES, IN COMBINATION WITH BASES.

Arseniates and arsenites.—When heated on charcoal in the interior blowpipe flame, arseniates and arsenites exhale the characteristic alliaceous odour of arsenic. If these salts are mixed with black flux, or else with cyanide of potassium and

| With Microcosmic Salt on the Platinum Wire. | | With Carbonate of Soda. |
|--|---------------------|---|
| Oxidating Flame. | Reducing Flame. | |
| A yellowish glass while hot, which is greenish when cold. | A fine green glass. | Not dissolved. |
| As with borax in both flames. | | Dissolves and is absorbed by the charcoal. |
| A transparent glass, which becomes translucent on cooling. | As with borax. | Not dissolved. Is reduced on charcoal, which becomes covered with a white sublimate of oxide. |

carbonate of soda, and the mixture heated in a glass tube closed at one end, a sublimate of metallic arsenic is formed, crystalline in its interior surface. It may be chased up the tube, becoming slowly oxidized. If the bottom of the tube is cut off, and the sublimed metal heated, it is converted into arsenious acid, which condenses as a white crystalline sublimate. (See page 108.)

Arseniurets, or compounds of metallic arsenic with other metals. — When arseniurets are heated before the blowpipe, in an open inclined tube, the arsenic volatilizes, oxidizes, and condenses in crystals as arsenious acid in the cool part of the tube. These crystals may then be treated with the usual tests for arsenious acid. (See pages 100 and 107.)

Antimoniurets afford a sublimate of oxide of antimony, when roasted in the open tube. When antimoniurets are heated on charcoal, the latter becomes covered with a white coating of oxide of antimony, not crystalline.

Borates. — When borates are fused with carbonate of potash on charcoal, and the mass moistened with sulphuric acid and alcohol, a green flame is generally, but not always, produced. If mixed in a finely powdered state with three or four times their weight of a flux, of one part of fluor spar and four and a half of bisulphate of potash (the mixture being moist), borates give a green flame for an instant, when held at the point of the blue flame on a platinum wire.

Bromides, when added to a bead of microcosmic salt nearly saturated with oxide of copper, and suddenly heated, communicate a blue or greenish blue colour to the flame. If heated with bisulphate of potash, in a glass tube sealed at one end, bromine vapour is evolved, and may be recognised by its yellowish red colour.

Chlorides, when treated with the glass of microcosmic salt and oxide of copper, as just described, communicate a bright blue or purplish blue colour to the flame.

Fluorides. — Those fluorides which contain water, disengage hydrofluoric acid when heated in a glass tube closed at one end. All fluorides, when mixed with bisulphate of potash or with microcosmic salt previously fused, and heated at the lower extremity of an open glass tube, (in contact with the flame,) evolve hydrofluoric acid, known by its corrosive action on glass, and its property of bleaching Brazil-wood test-paper.

The presence of silica in a mineral interferes with the detection of fluorine by the usual test of sulphuric acid, as described at page 124. But an indication of the existence of fluorine in such a substance may then be obtained by sub-

mitting it to the following operation. A small fragment of the mineral is heated to redness upon a piece of platinum foil, split into a glass tube of about six or eight inches in length, open at both ends. The tube is held obliquely, with the mineral close to the lower end, and a small blowpipe flame is directed into the tube. The moisture thus introduced with the flame carries away the gaseous fluoride of silicon from the mineral, and condenses in drops in the upper part of the tube. These drops, when afterwards evaporated by warming the tube throughout, leave a white spot, which consists of silica, proceeding from the decomposition of the fluoride of silicon by the water with which it condensed. (Berzelius.)

Iodides, when added to a bead of microcosmic salt nearly saturated with oxide of copper, and suddenly heated, give a fine emerald green colour to the flame. When iodides are heated with bisulphate of potash in a glass tube closed at one end, iodine vapour is evolved, and may be recognised by its purple colour and action on starch. (page 148.)

Nitrates. — Those which are fusible deflagrate on charcoal. Infusible nitrates, heated to redness in a glass tube, give off nitrous vapours. All nitrates give red vapours when mixed with bisulphate of potash and heated.

Phosphates. — The blowpipe tests for phosphoric acid are neither very characteristic nor delicate; therefore the humid tests for that acid are to be preferred. The following blowpipe test for a phosphate (sulphur and arsenic being absent) is suggested by Berzelius. The substance is fused with boracic acid on charcoal; when fused, the extremity of a steel wire is introduced into the bead, which is heated strongly in the interior flame. Borate and phosphuret of iron are formed. On breaking the fused mass (wrapped in paper) in a mortar, the phosphuret of iron is perceived, having the appearance of a metallic button, which affects the magnet and is brittle.

When the phosphoric acid in a mineral amounts to more than three per cent., it is said that it may be detected in the following manner: — A fragment of the mineral is moistened with strong sulphuric acid, and heated in a dark

room at the point of the interior flame, when the outer flame acquires a bluish-green colour, distinct from the green tints imparted by boracic acid, barytes, and copper. The mineral may be held by the platinum forceps. Some phosphoric minerals give a green tint to the outer flame without being moistened with sulphuric acid. (Fuchs and Erdmann.)

Seleniates and *selenites* give the characteristic odour of selenium, with soda on charcoal, in the interior flame. They behave like sulphates with the glass of silica and soda.

Seleniurets, in the exterior flame, evolve a strong odour resembling putrid horse-radish. When seleniurets are heated in the open tube, metallic selenium sometimes volatilizes and condenses. With the glass of silica and soda, seleniurets behave as seleniates and sulphates.

Silicic acid is characterized by dissolving easily in carbonate of soda with effervescence, giving a transparent and colourless bead, which remains transparent when cold, provided the carbonate is not in too large a proportion to the silicic acid. In a bead of microcosmic salt, silicic acid is almost insoluble, and floats about in a collected state as an opaque mass in the transparent bead. When silicates are heated with microcosmic salt, the bases are generally dissolved, and the silicic acid remains undissolved.

Sulphates. — If a sulphate is mixed with the colourless and transparent glass of silica and soda, and the mixture heated in the interior flame, the bead acquires a deep yellow or red colour, either immediately or on cooling. This test for sulphates is, of course, applicable to those only whose bases communicate no colour to a glass of silicate of soda: for others, the following character may be applied as a test. When a sulphate is heated on charcoal, in the reducing flame, with a mixture of two parts of soda and one part of borax, sulphuret of sodium is formed. The moistened mass tarnishes a bright piece of metallic silver; and if wetted with a few drops of dilute sulphuric acid, exhales the odour of sulphuretted hydrogen. With each of these tests, compounds of selenium behave in the same way as sulphates;

therefore the absence of selenium should first be proved, by heating the substance on charcoal, to discover whether the peculiar odour of selenium is exhaled.

Sulphurets. — When heated in an open inclined tube, sulphurets evolve sulphurous acid gas, which is recognised by its odour and by its property of bleaching moist Brazil-wood paper. Sulphurets also exhale the odour of sulphurous acid when heated on charcoal in the exterior flame. With the glass of silica and soda, and also with that of borax and soda, on charcoal, sulphurets behave like sulphates, seleniates, and seleniurets.

Tellurets give, when roasted in the inclined open tube, a sublimate of a white powder, which, when heated, first fuses into colourless drops, and then sublimes.

SECTION III.

COURSE OF BLOWPIPE OPERATIONS TO BE PERFORMED ON AN UNKNOWN SUBSTANCE.

First Operation. — The substance is heated in a glass tube, sealed at one end.

| | | |
|---|---|---|
| (a) Salts volatilized and condensed on the cool part of the tube. | <div>Ammoniacal salts.</div> <div>Most salts of mercury.</div> <div>Many chlorides of fixed oxides.</div> | <div>They mostly sublime without decomposition, unless they contain a fixed acid.</div> <div>If heated with dry carbonate of soda, mercurial salts yield a sublimate of metallic mercury. (page 94.)</div> |
| (b) Oxides and acids sublimed. | <div>Oxide of antimony.</div> <div>Arsenious acid.</div> <div>Arsenic acid.</div> <div>Oxide of tellurium.</div> <div>Osmic acid.</div> | <div>Sublimes without previous fusion.</div> <div>Condenses in white octahedral crystals.</div> <div>Becomes converted into oxygen gas and arsenious acid.</div> <div>Fuses previous to subliming.</div> <div>Recognised by its odour.</div> |
| (c) Acids and ammonia volatilized. | <div>Ascertained by their action on red and blue litmus paper.</div> | |
| (d) Metals volatilized. | <div>Tellurium.</div> <div>Cadmium.</div> <div>Mercury.</div> <div>Arsenic.</div> | <div>Volatile only at a bright red heat.</div> <div>Gives a yellowish-red coating to charcoal when heated on it in the open air.</div> <div>Condenses in liquid drops.</div> <div>The interior surface of the sublimate is crystalline. The odour of garlic is evolved.</div> |
| (e) Water. | Condenses on the cold sides of the tube. | |
| (f) Sulphur. | A yellow sublimate, inflammable at a low temperature. | |
| (g) Selenium. | Characterized by the odour of its vapour. | |
| (h) Organic bodies. | Become black, leaving a residue of charcoal. | |

Second Operation. — *The substance is heated in an inclined glass tube, open at both ends.*

| | | | | |
|------------------------------|---|----------------------|---|--|
| (a) White sublimates formed. | { | Oxide of antimony. | { | Formed during the roasting of metallic antimony, sulphuret of antimony, and of metallic antimonurets; also by heating oxide of antimony. |
| | | Arsenious acid. | | Formed by the roasting of arseniurets. |
| | | Oxide of bismuth. | | Formed by the roasting of sulphuret of bismuth and alloys of bismuth. The sublimate melts into brownish or yellowish drops when heated. |
| | | Chloride of lead. | | Melts readily when heated. |
| | | Oxide of lead. | | Accompanying bodies which form volatile oxides or acids. |
| | | Selenite of lead. | | From roasting the seleniuret. |
| | | Sulphate of lead. | | From roasting the sulphuret. |
| | | Mercurial compounds. | | |
| | | Molybdic acid. | | Sublimes partly in the state of shining pale yellow crystals. |
| | | Oxide of tellurium. | | From metallic tellurets. |
| (b) Odours exhaled. | { | Sulphurous acid. | { | From metallic sulphurets. |
| | | Selenium. | | From metallic seleniurets. A red sublimate of selenium is sometimes formed. |
| | | Arsenic. | | From a few arseniurets only. |

Third and Fourth Operations.— *The substance is heated alone, in the open air, first upon charcoal, and afterwards between the platinum points of a pair of forceps, or upon platinum foil.*

- (a) Oxides and acids which are fused. { Antimony, oxide of; bismuth, ox. of; copper, ox. of; lead, ox. of; molybdic acid; tellurous acid; vanadic acid.
- (b) Oxides and acids which do not fuse. { Alumina; antimonious acid; barytes; cadmium, ox. of; cerium, perox. and protox. of; chromium, ox. of; cobalt, ox. of; glucina; iron, perox. of; lime; magnesia; manganese, perox. of; nickel, ox. of; silica; strontian; tantallic acid; tin, perox. and protox. of; titanlic acid; tungstic acid; uranium, perox. and protox. of; yttria; zinc, ox. of; zirconia.
- (c) Colours which may be imparted to the flame. {
 Blue or blueish. { Chloride and bromide of copper; lead; arsenic; selenium; antimony.
 Green or greenish. { Zinc; barytes; boracic acid; tellurium; copper; phosphoric acid; ammonia.
 Red or crimson. { Lime; strontian; lithia; potash.
 Yellow. { Soda; water.
- (d) Substances which may be volatilized. {
 Metals. { Produce a sublimate on charcoal. { Antimony; arsenic; bismuth; cadmium; lead; tellurium; tin; zinc.
 { Give no sublimate on charcoal — mercury; osmium.
 Compounds of mercury.
 Oxides of volatile metals, in the reducing flame.
 Sulphur; selenium; iodine; bromine.
 Many chlorides and iodides.
- (e) Substances which change their colour on ignition. {
 Red oxide of mercury, minium, and most chromates are black when hot, and red or yellow when cold.
 Oxide of zinc and titanlic acid are yellow when hot, and white when cold.

[The dissimilar action of the exterior and interior flames must be particularly observed.]

Fifth Operation. — Heating with reagents.

1. With carbonate of soda.

- (a) Substances which are fusible with soda on the platinum wire in the oxidating flame. { Oxide of antimony; oxide of chromium; oxide of cobalt; oxide of copper; oxide of lead; oxides of manganese; molybdic acid; silica; oxide of tellurium; titanitic acid; tungstic acid; vanadic acid.
- (b) Substances which are fusible with soda on charcoal, giving a clear bead. { Silicic acid, with evolution of carbonic acid gas. { Giving a yellow glass white hot, which is opaque when cold.
Titanic acid.
- (c) Metals whose compounds are reducible with soda on charcoal in the reducing flame. { Metals the oxides of which form a sublimate on the charcoal. { Antimony; arsenic; bismuth; cadmium; lead; selenium; tellurium; zinc.
Metals which deposit no sublimate on the charcoal. { Cobalt; copper; gold; iron; molybdenum; nickel; platinum; silver; tin; tungsten.
- (d) Substances which are neither fused nor reduced with soda on charcoal. { Alumina; barytes; oxides of cerium; glucina; lime; magnesia; strontian; tantalitic acid; thorina; oxides of uranium; yttria; zirconia.
- (e) Examine for sulphur and selenium by the glass of silica and soda.

2. With borax, on the platinum wire, in both flames. The colours of the beads produced by the various metallic oxides, are as follow : —

| In oxidating flame. | | In reducing flame. | |
|------------------------|------------------------------|--------------------|---------------------------|
| Colourless | Alumina | Colourless | Alumina |
| | Antimony, ox. of (when cold) | | Barytes |
| | Barytes | | Cadmium, ox. of |
| | Bismuth, ox. of (when cold) | | Cerium, ox. of |
| | Cadmium, ox. of (when cold) | | Glucina |
| | Glucina | | Lanthanum, ox. of |
| | Lime | | Lime |
| | Lanthanum, ox. of | | Magnesia |
| | Magnesia | | Manganese, ox. of |
| | Molybdic acid (when cold) | | Silica |
| | Silicic acid | | Strontian |
| | Strontian | | Tantallic acid |
| | Silver, ox. of | | Thorina |
| | Tantallic acid | | Tin, ox. of |
| | Tellurium, ox. of | | Yttria |
| | Thorina | | Zinc, ox. of |
| | Tin, ox. of | | Zirconia. |
| | Titanic acid | Reddish brown | Copper, ox. of |
| | Tungstic acid (when cold) | | Molybdic acid |
| Red, or reddish yellow | Yttria | Yellow | Vanadic acid (while hot). |
| | Zinc, ox. of | | Tungstic acid |
| | Zirconia. | | Titanic acid (while hot). |
| | | | |
| Red, or reddish yellow | Cerium, ox. of (while hot) | Green | Chromium, ox. of |
| | Chromium, ox. of (while hot) | | Iron, ox. of |
| | Iron, ox. of | | Uranium, ox. of |
| | Nickel, ox. of (when cold). | | Vanadic acid (when cold). |
| Yellow | Antimony, ox. of (while hot) | Blue | Cobalt, ox. of. |
| | Bismuth, ox. of (while hot) | | |
| | Cadmium, ox. of (while hot) | | |
| | Lead, ox. of (while hot) | | |
| | Molybdic acid (while hot) | | |
| | Uranium, ox. of | | |
| | Vanadic acid. | | |

| | In oxidating flame. | | In reducing flame. |
|--------|---|------|--|
| Green | { Chromium, ox. of (when cold) Copper, ox. of (while hot). | Grey | { Antimony, ox. of Bismuth, ox. of Nickel, ox. of Silver, ox. of Tellurium, ox. of |
| Violet | { Manganese, ox. of Nickel, ox. of (while hot). | | |
| Blue | Cobalt, ox. of | | |

3. With microcosmic salt, on the platinum wire, in both flames.

The colours imparted to a bead of microcosmic salt by various metallic oxides are as follow: —

| | In oxidating flame. | | In reducing flame. |
|------------|--|----------------------------|---|
| Colourless | { Alumina Antimonious acid Barytes Bismuth, ox. of (when cold) Cadmium, ox. of Glucina Lanthanum, ox. of Lead, ox. of (when cold) Lime Magnesia Molybdic acid Strontian Tantalac acid Tellurium, ox. of Thorina Tin, ox. of Titanic acid Tungstic acid Yttria Zinc, ox. of Zirconia. | Colourless | { Alumina Barytes Cadmium, ox. of Cerium, ox. of Glucina Lanthanum, ox. of Lime Magnesia Manganese, ox. of Strontian Tantalac acid Thorina Tin, ox. of Yttria Zinc, ox. of Zirconia. |
| Red | { Cerium, ox. of (while hot) Iron, ox. of Nickel, ox. of (while hot) Chromium, ox. of (while hot). | Red or reddish brown | { Antimonious acid with iron Chromium, ox. of (while hot) Copper (when cold) Nickel, ox. of (while hot) Titanic acid with iron Tungstic acid with iron. |
| | | Yellow | { Titanic acid (while hot). |

| | In oxidating flame. | | In reducing flame. |
|--------|--|--------|---|
| Yellow | { Bismuth, ox. of (while hot) Lead, ox. of (while hot) Silver, ox. of Uranium, ox. of (while hot) Vanadic acid. | Green | { Chromium, ox. of (when cold) Copper, ox. of (while hot) Iron, ox. of Molybdic acid (when cold) Uranium, ox. of Vanadic acid (when cold). |
| Green | { Copper, ox. of (while hot) Molybdic acid Uranium, ox. of (when cold) Chromium, ox. of (when cold). | Blue | { Cobalt, ox. of Molybdic acid (while hot) Tungstic acid. |
| Violet | Manganese, ox. of | Violet | { Titanic acid (when cold). |
| Blue | Cobalt, ox. of | Brown | { Vanadic acid (while hot). |
| | | Grey | { Antimony, ox. of Bismuth, ox. of Lead, ox. of Silver, ox. of Tellurium, ox. of |

CHAPTER VIII.

QUALITATIVE ANALYSIS OF A GASEOUS MIXTURE.

I. TABULAR VIEW OF THE PRINCIPAL PROPERTIES OF SOME GASES.

| | | | | | |
|----------------------------|---|------------------------------|---|---------------------|-----------------------|
| Oxygen | - | } Re-inflame a glowing taper | - | } Soluble in water. | } Absorbed by potash. |
| Nitrous oxide | - | | - | | |
| Ammonia | - | - | - | | |
| Hydrochloric acid | - | - | - | | |
| Chlorine | - | - | - | | |
| Sulphurous acid | - | - | - | | |
| Carbonic acid | - | - | - | | |
| Sulphuretted hydrogen | - | - | - | | |
| Cyanogen | - | - | - | | |
| Olefiant gas | - | - | - | | |
| Phosphuretted hydrogen | - | - | - | } Combustible. | |
| Arsenietted hydrogen | - | - | - | | |
| Carbonic oxide | - | - | - | | |
| Hydrogen | - | - | - | | |
| Light carburetted hydrogen | - | - | - | | |

II. COURSE OF THE QUALITATIVE ANALYSIS OF A GASEOUS MIXTURE; THE CONSTITUENTS BEING MENTIONED IN THE FOLLOWING LIST: —

- | | |
|---------------------------|--------------------------------|
| 1. Carbonic acid | 10. Oxygen |
| 2. Hydrochloric acid | 11. Nitrous oxide |
| 3. Chlorine | 12. Nitric oxide |
| 4. Sulphurous acid | 13. Light carburetted hydrogen |
| 5. Sulphuretted hydrogen | 14. Olefiant gas |
| 6. Cyanogen | 15. Carbonic oxide |
| 7. Phosphuretted hydrogen | 16. Hydrogen |
| 8. Arsenietted hydrogen | 17. Nitrogen. |
| 9. Ammonia | |

(A). Into the dry gas contained over mercury, introduce, first, moistened sticks of potash; after a little while, withdraw the potash, and dissolve it in water.

The first six of the above list are absorbed.

- | | | |
|--|---|--|
| 1. <i>Carbonic acid.</i> | { | Remove the more soluble gases from a portion of the original gas by water, and apply the test of lime-water to the residue. (See page 123.) |
| 2. <i>Hydrochloric acid,</i> and 3. <i>Chlorine.</i> | | Neutralize the solution of the potash by pure nitric acid, and test with nitrate of silver. (See page 136.) Chlorine and hydrochloric acid are distinguished from each other by the power of the first to bleach vegetable colours, which property is not possessed by hydrochloric acid. |
| 4. <i>Sulphurous acid.</i> | { | Peroxide of lead, if agitated in the original gas, absorbs sulphurous acid. |
| 5. <i>Sulphuretted hydrogen.</i> | | The solution of the potash produces a black precipitate in salts of lead. |
| 6. <i>Cyanogen.</i> | { | To the solution of the potash apply the test of peroxide and protoxide of iron (Scheele's test), page 143. |

(B). After the removal of the potash, transfer the remaining gas to another jar, and introduce into it a solution of nitrate of silver. Nos. 7, 8, and 9. are absorbed.

- | | | |
|-----------------------------------|---|---|
| 1. <i>Phosphuretted hydrogen.</i> | { | Combustible; producing white fumes of phosphoric acid: this gas is sometimes spontaneously inflammable. |
| 2. <i>Arsenitied hydrogen.</i> | | Gives a volatile deposit of metallic arsenic when passed through a red-hot tube. |
| 3. <i>Ammonia.</i> | { | Known by its great solubility in water, its odour, and its alkaline reaction. |

(C). The gases which remain after the action of potash, and of nitrate of silver, are, Nos. 10, 11, 12, 13, 14, 15, 16, and 17.

1. Introduce a stick of phosphorus into the gas, and allow it to remain so long as any contraction occurs. *Oxygen* is absorbed.*

2. If the gas supports combustion before, but not after, agitation with water, it contains *nitrous oxide*.

(D). Into a *portion* of the remaining gas contained in a tube through which the electric spark can be passed†, pass up an equal volume of pure *oxygen*.

* Phosphorus does not act upon oxygen in the presence of olefiant gas, unless the pressure be greatly reduced. Phosphorus is likewise without action on perfectly pure oxygen.

† Such as Dr. Ure's eudiometer, of which a figure is given under the subject of Eudiometry.

1. The production of ruddy fumes shows the presence of *nitric oxide*.

2. Pass the electric spark* ; if explosion takes place, Nos. 13, 14, 15, and 16. may be present.

(E). To the other portion of the gas (not mixed with oxygen), add half its own bulk of pure *chlorine*, and keep the mixture in a dark place.

Contraction and formation of oily drops show the presence of *olefiant gas*, or *vapours of hydrocarbons*.

After allowing the mixture to stand for about twenty-four hours, withdraw the excess of chlorine by agitation with solution of potash, and heat *potassium* in the residue so long as contraction occurs.†

Carbonic oxide is absorbed by the potassium.

To the residue add twice its bulk of oxygen, and pass the electric spark. If explosion takes place, both light carburetted hydrogen and hydrogen may have been present. *Carburetted hydrogen* produces its own volume of carbonic acid. By ascertaining, (1.) the volume of the gas before adding oxygen ; (2.) the amount of oxygen added ; (3.) of carbonic acid produced ; and (4.) of oxygen in excess (by removing it afterwards by phosphorus), the presence and quantity of *hydrogen* may be calculated. (See the following Table.)

As nitrous oxide interferes with the above process, it must be previously removed by agitation with water. If any gas remains after detonation and absorption of carbonic acid by potash, and of oxygen by phosphorus, this must be *nitrogen*.

* The combination of oxygen with the combustible gases may also be caused by the introduction of small pellets of spongy platinum. This method is generally more convenient than by passing the electric spark.

† This operation is best performed in a glass tube closed at one end, about eight inches in length, with one inch and a half from its top recurved to hold the potassium.

III. ANALYSIS OF COAL-GAS.

In the following method of analyzing coal-gas, the olefiant gas and vapours of hydrocarbon are estimated together as the contraction by chlorine. The determination of the hydro-carburetted vapours may be accurately effected, as shown by Mr. Faraday, by means of oil of vitriol. That liquid absorbs both the vapours and olefiant gas, but the latter not so rapidly as the former; and if the coal-gas is diluted with three or four times its volume of atmospheric air or hydrogen, and the mixture kept in the shade, the absorption of olefiant gas is prevented. Another portion of the gas under examination may be taken for the remaining operations.

As the principal luminiferous constituents of coal-gas are olefiant gas and the vapours of hydrocarbons, a good approximation to its true value may be obtained by determining merely the contraction which the gas experiences when mixed with chlorine, neglecting the other operations in the following method of analysis; and instead of removing the excess of chlorine by caustic potash, at the close of the experiment, the amount of chlorine absorbed by water in similar circumstances may be noted, and deducted from the entire condensation. The necessity of carefully excluding the mixture from solar light, arises from the property which chlorine possesses of condensing carbonic oxide under the influence of solar light and moisture; but no condensation from the presence of carbonic oxide takes place in the dark, or in candle-light. The purity of the chlorine employed in this process should be previously ensured by ascertaining whether it is absorbed by water, or by a dilute alkaline solution, without leaving a residue. The chlorine should be added to the gas so long as the volume of the latter diminishes.—(*Applied Chemistry: art. on Gas Illumination.*)

Analysis of Coal-gas (Qualitative and Quantitative).

The constituents to be estimated are, carbonic acid, olefiant gas and vapours of hydrocarbons, carbonic oxide, light carburetted hydrogen, hydrogen, and nitrogen.

Agitate the gas in a graduated jar with a solution of caustic potash.

Carbonic acid is absorbed by the solution of potash.

Transfer the remaining gas to another graduated jar, of about half an inch in diameter, standing over water; mix it with half its bulk of pure chlorine, and keep the mixture carefully protected from the solar rays.

Olefiant gas and vapours of hydrocarbons are absorbed. The condensation is complete in the course of 24 hours.

Remove the excess of chlorine from the remaining gas by agitation with a solution of caustic potash, and note the bulk of the residue. Heat potassium gently in some of the remaining gas contained in a recurved tube over mercury.

Carbonic oxide is absorbed by the potassium.

Transfer a portion of the remainder into the eudiometer, and introduce a known measure of pure oxygen (not less than twice the volume of the gas), and detonate by the electric spark. Note the quantity of gas, and introduce into it a solution of caustic potash.

Carbonic acid, equal in bulk to the quantity of *light carburetted hydrogen*, is absorbed.

The residue consists of nitrogen and the excess of oxygen. Introduce phosphorus to absorb oxygen, that the *amount of oxygen employed in the combustion* may be found. From this amount deduct twice the volume obtained of light carburetted hydrogen; twice the bulk of the remaining oxygen employed in the combustion represents that of the *hydrogen*. The residuary gas is *nitrogen*.

CHAPTER IX.

DETECTION OF POISONS IN ORGANIC MIXTURES.

WHEN an inorganic poison is presented for examination unmixed with organic matters, its composition may be ascertained by processes already described; but if the poison is to be looked for in the contents of the stomach, or any such organic mixture, its properties may have become so masked, its composition so altered, and the usual action of reagents so restrained, as to require a modification of the processes employed where organic matters are absent. In general, it is not convenient, in these examinations, to follow the course recommended in mineral qualitative analysis, of determining the presence or absence of certain classes of bodies, and afterwards proceeding to individual substances; but better to seek at once for a particular substance, by the application of its appropriate test. This plan is adopted for two reasons: first, because the act of poisoning is almost always committed with a single substance; and second, because there usually exist evidences, of a physiological or circumstantial character, which have excited a suspicion of the true nature of the poison; the appropriate tests for which are then applied.

The substances for the discovery of which, in organic mixtures, processes will be described, are the following: —

- | | |
|----------------|----------------------|
| 1. Arsenic | 7. Sulphuric acid |
| 2. Mercury | 8. Hydrochloric acid |
| 3. Antimony | 9. Oxalic acid |
| 4. Copper | 10. Hydrocyanic acid |
| 5. Lead | 11. Alcohol. |
| 6. Nitric Acid | |

1. *Arsenic.*

The ordinary liquid tests for arsenic can seldom be sufficiently depended on in organic solutions. In the presence of organic matters, the only unequivocal tests for arsenic are certain processes of reduction, whereby *metallic arsenic* itself is obtained. These reduction processes are of three kinds: one consists in the *precipitation of metallic arsenic from a liquid containing arsenious acid or arsenic acid, by metallic copper*; in another, *arsenietted hydrogen gas is evolved from a liquid containing arsenic, and is afterwards decomposed*; and in the process of the third kind, *metallic arsenic is obtained in the dry way, from sulphuret of arsenic*, the latter being obtained by precipitation from a liquid by sulphuretted hydrogen.

I. The first of these methods of testing for arsenic has been recently introduced by M. Reinsch, and is hence distinguished as Reinsch's test. It is conducted in the following manner. The liquid suspected to contain arsenic is first strongly acidulated with hydrochloric acid (previously ascertained to be free from arsenic); a perfectly clean plate of metallic copper is then introduced into the acidified mixture, and the liquid is heated to the boiling point. If any arsenic is present, even no more than the millionth part of the liquid, the copper soon becomes covered with a steel-gray crust of metallic arsenic. After the lapse of a quarter of an hour, or half an hour, the precipitation of arsenic is complete. But arsenic is not the only metal which might be precipitated on the plate of copper in such circumstances. The various precious metals (silver, gold, platinum, &c.), bismuth and antimony, also afford deposits on the copper, differing certainly in appearance from that produced by arsenic, but sufficiently similar to the latter to render the further examination of the metallic deposit, absolutely essential.

The plate of copper is removed from the liquid, washed first with weak hydrochloric acid, and then with water, and dried. The drying should be done very cautiously, to prevent

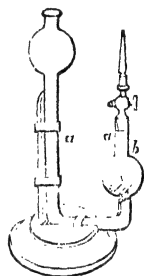
the volatilization of the arsenic. The part of the plate of copper on which the arsenic is deposited is then cut into chips, all of which, if the crust is not abundant, are placed in such a tube as *c* (figured at page 108.), and heated to low redness. The arsenic then volatilizes and oxidizes, and arsenious acid condenses on the side of the tube in octohedral crystals, the equilateral triangular faces of which are observable by a magnifier of four or five powers. Larger crystals may be obtained by removing the copper chips, and chasing the sublimate up and down the tube by the flame of a spirit lamp, the open end of the tube being closed by the finger. The form of the crystals having been observed, a little distilled water is introduced into the tube to dissolve the sublimate, and the solution is divided into three parts: one portion is mixed with pure hydrochloric acid, and tested for arsenious acid with sulphuretted hydrogen (p. 101.); another portion is treated with the ammonio-nitrate of silver (p. 100.); and the third with ammonio-sulphate of copper. (p. 107.) Antimony, if deposited upon the plate of copper, would also afford a white sublimate on the sides of the tube; but that sublimate is not nearly so volatile or so crystalline as arsenious acid, and, unlike the latter, is insoluble in water; therefore the indications of ammonio-nitrate of silver and ammonio-sulphate of copper, with the aqueous solution of the sublimate, are perfectly conclusive as regards the presence or absence of arsenic.

This test for arsenic is as applicable to an organic liquid as to a pure solution of arsenious acid. Organic fluids are prepared for this process by being simply boiled for half an hour with a little hydrochloric acid, and filtered, if any solid particles are diffused through the liquid. Organic solids are mixed with diluted hydrochloric acid, and the mixture is boiled for about half an hour, when the liquid is filtered, unless complete solution has taken place. The liquid is then ready to receive the copper. Dr. Christison suggests the use of copper leaf in this process, in the place of sheet copper. Phosphoric, sulphuric, or acetic acid may not be used instead of hydrochloric acid. So long as

the hydrochloric acid is in decided excess, it does not appear that its proportion affects the delicacy of the test. The hydrochloric acid may be as little as one thirtieth or as much as one half of the whole liquid.

II. The principle of the second method of testing for arsenic to be here noticed is, that whenever hydrogen gas is evolved in contact with a soluble arsenical compound, the arsenic unites with hydrogen, forming arseniethed hydrogen gas, in which the existence of arsenic is easily demonstrated. The arrangement represented in the figure was contrived by Mr.

Fig. 16.



Marsh, for the operation adverted to. The stopcock, which can be fitted to the tube by means of a cork, being removed, a few fragments of pure zinc are introduced into the lower bulb, and dilute sulphuric acid is poured upon them, up to the mark *a*. Hydrogen gas is evolved, with which the whole limb *b* is soon filled, on closing the stopcock, the acid liquid being then forced into the upper bulb. As the zinc and also the sulphuric acid of commerce almost always contain some arsenic, it is necessary to examine whether the hydrogen is free from arsenic, or not. For that purpose the gas is kindled at the jet, and allowed to burn with a small flame. On holding the bottom of a porcelain bason or a stoneware plate *in the flame*, a black spot, of a bright metallic lustre, will immediately be formed on it, in the centre of the flame, if the gas contains any, even a very small amount of arsenic. Another method of discovering the presence of arsenic in the gas, is to hold a piece of coloured glass *over* the flame, when the glass becomes covered with a white sublimate of arsenious acid, if any arsenic is present. If the hydrogen gas presents these appearances, some arsenic (or antimony or bismuth) must have existed either in the acid or the zinc; but if it does not, pour off some of the dilute sulphuric acid, and mix with the remainder a portion of the liquid to be tested. Proceed as before to collect the gas, and burn it against

a stoneware plate, and under a piece of coloured glass, as before directed.

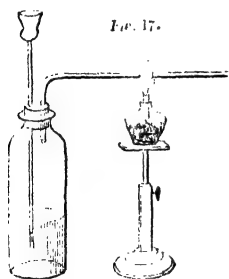
If no black spot appears upon the stoneware plate, when held in the flame, and no white sublimate upon the coloured glass plate, when held above the flame, conclusive evidence is afforded of the absence of arsenic, at least in a soluble state. But the formation of a metallic spot and of a white sublimate are not as conclusive of the presence of arsenic, since somewhat similar black spots and white sublimates are afforded by antimony, and, when the evolution of gas is very brisk, by bismuth. Organic matters might also cause the formation of a black spot upon a porcelain bason held in the flame; and a porcelain bason having a lead glaze might acquire a black mark by exposure to a pure hydrogen flame, through the reduction of oxide of lead in the glaze.

When the apparatus just described is employed, one method of determining the presence of arsenic conclusively is by collecting and examining the white sublimate formed by the combustion of the gas. For this purpose, the sublimate is collected within a glass tube, open at both ends, held slightly oblique. This tube may be about six inches in length, and half an inch in diameter. When the sublimate produced by the combustion of two or three times the contents of a bulb of the apparatus has been obtained, it may be treated with a little water, when it slowly dissolves, if it is arsenious acid, giving a solution in which arsenic is easily recognised by the three principal fluid tests for arsenious acid, — namely, sulphuretted hydrogen (hydrochloric acid being added), ammonio-nitrate of silver, and ammonio-sulphate of copper. If the metal is antimony or bismuth, the proper indications which these reagents give with arsenious acid (mentioned at pages 100, 101. and 107.) are not perceived.*

* If the liquid under examination contains both arsenic and antimony, the white sublimate may consist of the arsenite of antimony, which is insoluble in pure water. If such is the case, the sublimate is dissolved in very dilute solution of potash, and the solution is treated, first, with sulphuretted hydrogen, and after-

A spot of metallic arsenic on the porcelain plate may be distinguished, and even separated from metallic antimony and metallic bismuth, by a solution of chloride of soda, or of chloride of lime, which dissolves the arsenic, but leaves both antimony and bismuth untouched.

Instead of burning the gas in the way described, it may be passed through a hard glass tube, a portion of which is heated red hot by a spirit lamp, by which all the arsenic in the gas is reduced to the metallic state and deposited in the tube, near the flame of the lamp. For this purpose a horizontal glass tube may be attached by a cork to the jet of the apparatus shown at fig. 16. (p. 275.); or an apparatus similar to that re-

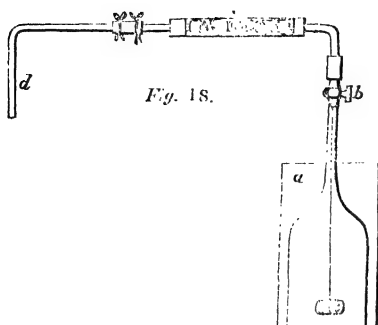


presented in the annexed figure may be employed. The funnel is for adding more acid or suspected liquid. This modification of the process just described is more manageable, and equally satisfactory. It may be left in action without requiring the constant presence of the operator; and the whole amount of arsenic originally contained in the liquid operated on, may be obtained in the tube without loss. When sufficient metal for examination has been collected, the tube may be removed, and replaced by another similar one. The manner of examining the metallic crust is described below.

Another and a preferable form of apparatus for the same purpose is represented in fig. 18. It consists of a cylindrical glass vessel *a*, containing a capped bell jar with an elongated neck, which is furnished with a stopcock *b*. A fragment of pure zinc is suspended from the stopcock by a string or wire: *c* is a stout glass tube, filled with cotton wool or asbestos,

wards with an excess of bicarbonate of ammonia. The antimony is thereupon precipitated as sulphuret, while sulphuret of arsenic remains in the ammoniacal solution, and may be precipitated by the addition of an excess of hydrochloric acid.

connected with the stopcock by a small tube and two perforated corks, and by another small tube and caoutchouc joint to a narrow bent tube of hard glass *d*,



in which the metallic arsenic is condensed. The use of the tube containing cotton or asbestos is to prevent the mechanical projection of minute drops of the liquid from the jar. The absence of arsenic in the

zinc and sulphuric acid having been already ensured, the liquid to be tested is mixed with sulphuric acid and introduced into the apparatus, the stopcock being open. When the liquid has filled the interior jar, the stopcock is closed, and the jar is allowed to become nearly full of gas, the liquid being driven back through the lower opening of the bell jar into the outer cylinder. A part of the tube is now heated to redness by a spirit lamp; the open extremity of the tube is placed beneath some water, in order to give an indication of the rapidity with which the gas passes when the stopcock is opened, and the cock is turned a little, so as to allow the gas to escape in slowly successive bubbles. When the bell jar becomes again filled with the liquid, the stopcock is closed, and not opened until the jar is nearly refilled with gas. The experiment is conducted in this manner until a sufficient quantity of the metallic deposit has been obtained for testing. The tube with the metal may then be detached from the apparatus, and replaced by another, if the whole of the arsenic in the liquid is to be collected without loss.

The metallic deposit of arsenic is distinguishable from the deposits of antimony and bismuth by several characters. 1. In the first place, arsenic is much more volatile than either of the other metals, so that it is not deposited in the hot part of the tube, as are the other metals, but a little beyond the heated part. If a very strong heat is applied, however,

antimony is not deposited on the hottest part, but on both sides of it; arsenic is deposited only on one side. 2. The following mode of determining the nature of the metallic crust (proposed by M. Fresenius) affords very satisfactory results. A gentle stream of dry sulphuretted hydrogen gas is passed through the tube containing the deposit, which is heated by a spirit lamp, from the farther end to the nearer, progressively. The metal, whether arsenic or antimony, thereby becomes converted into a sulphuret, which is yellow in the case of arsenic, and orange (or gray, if strongly heated,) in that of antimony. To distinguish between these sulphurets, a stream of dry hydrochloric acid gas is next passed through the tube, without the application of heat: sulphuret of antimony wholly disappears almost instantly; chloride of antimony volatilizes, and may be conveyed into water, and tested by sulphuretted hydrogen, &c.: sulphuret of arsenic, on the contrary, is not affected by hydrochloric acid, and may be obtained in solution, by introducing a small quantity of ammonia into the tube. This ammoniacal liquid yields a yellow precipitate of sulphuret of arsenic when supersaturated with hydrochloric acid. 3. An easier and quite as satisfactory a method of detecting the presence of arsenic in the metallic crust, is to place a portion of the crust, or a portion of the tube, into a wide tube sealed at one end, and apply the heat of a spirit lamp. If arsenic is present, it volatilizes and oxidizes, and octohedral crystals of arsenious acid condense on the sides of the tube, which may be examined as already directed, at page 274. 4. Another method of distinguishing between metallic arsenic and other metals, is the following:—The metal is dissolved in a small quantity of fuming nitric acid, and the solution is evaporated to dryness by means of a water-bath. If arsenic is present, the residue contains arsenic acid, which is soluble in water, and its solution gives a brick-red precipitate when mixed with ammonio-nitrate of silver. Antimonic and antimonious acids, which are formed by the action of nitric acid on antimony, are insoluble in water.

Various other methods of distinguishing arseni-
tied hy-

drogen from antimonietted hydrogen have been pointed out, only two of which need be alluded to here. One of these consists in passing the gas through an alcoholic solution of a caustic alkali, — either potash, soda, or ammonia. Antimonietted hydrogen is thereby decomposed, and metallic antimony is deposited in brownish-black flakes. But arsenietted hydrogen undergoes no perceptible change. The bulbed tube known as Liebig's potash apparatus (figured under the subject of Organic Analysis) may be employed in the operation. If a sufficient quantity of the alcoholic solution is employed, the antimonietted hydrogen may be completely absorbed and decomposed. (Dr. Meissner.) The other method consists in exposing the gas to pure and concentrated nitric acid in a "Liebig's bulbed apparatus." The acid absorbs and oxidizes the metal contained in the gas, whether arsenic or antimony, and when evaporated to dryness leaves a residue of arsenic acid or one of the oxides of antimony. The residue is treated with water, and the solution tested for arsenic acid by ammonio-nitrate of silver. (M. Meillet.)

In testing an organic liquid for arsenic by Marsh's test, no small inconvenience is generally experienced from the quantity of froth produced, for the subsidence of which, long repose is necessary. But the disengagement of froth may be prevented or greatly lessened by destroying the various organic matters present, previous to the application of the test. The following mode of decomposing the organic matters was proposed by MM. Danger and Flandin, and has received the sanction of M. Regnault. The material is first brought to a state of dryness at a moderate heat, and is then digested with from one fifth to one fourth of its weight of concentrated sulphuric acid, and the carbonaceous mass is heated, and occasionally stirred, until dry, when it has the appearance of charcoal. The mass is then treated with a little nitric acid or aqua regia, to dissolve the arsenic, and washed with water. The washings, which contain the whole of the arsenic, are lastly concentrated by evaporation, mixed with sulphuric acid, and tested for arsenic in Marsh's appa-

tus. If the organic substance contains much common salt, a little of the arsenic may be lost during the carbonization, being volatilized as chloride. But if the process of carbonization is conducted in a retort connected with a cooled receiver, the whole of the volatilized chloride condenses and is collected in the receiver.

III. Another process for the detection of arsenic in an organic mixture, differing in kind from either of the preceding, remains to be briefly adverted to. It consists in separating the arsenic as sulphuret, and in decomposing that sulphuret with liberation of metallic arsenic. The course of examination of an organic liquid or solid, by this test, presents three stages: 1°, the preparation of the material; 2°, the separation of the arsenic, as sulphuret, by sulphuretted hydrogen; and 3°, the reduction of the sulphuret of arsenic.

(A). *Preparation of the material.* — The preparation of an organic material for exposure to sulphuretted hydrogen is a subject which has received considerable attention, and several modes of procedure have been pointed out. Three of these processes are as follow: —

1. The matters are first boiled for a considerable time with water and a small quantity of nitric acid, and the mixture is then strained through a piece of calico. The animal matter in the filtered liquid is precipitated by the addition of an excess of nitrate of silver; and the excess of nitrate of silver is decomposed by adding common salt to the mixture. The liquid is then passed through a paper filter.

By treatment with nitric acid, chlorine, and several other oxidizing agents, *arsenious acid* is converted into *arsenic acid*. Now a solution of *arsenic acid* is precipitated by sulphuretted hydrogen with less facility than a solution of *arsenious acid*; a trace of *arsenic acid* may even effectually resist decomposition by sulphuretted hydrogen. When the arsenic, therefore, can be contained in a suspected liquid in the state of *arsenic acid* (as it may, partly or entirely, in the above process), it should be reduced to the state of *arsenious acid* before being exposed to sulphuretted hydrogen. This may be readily

effected by sulphurous acid at a boiling heat. (Wöhler.) An aqueous solution of sulphurous acid is mixed with the suspected liquid, and the mixture boiled; by this, the arsenic acid is reduced, while the excess of sulphurous acid is expelled in the ebullition. Sulphuretted hydrogen may then be passed through the solution. The sulphuric acid employed in the preparation of the sulphurous acid must be perfectly free from arsenic, otherwise the sulphurous acid will be found to contain traces of arsenic.

2. The following mode of preparing organic matters for treatment with sulphuretted hydrogen is recommended by MM. Duflos and Hirsh.* The suspected mass, as the stomach with its contents, for instance, is digested in a tubulated retort, with an equal weight of hydrochloric acid, previously ascertained to be free from arsenic by the test of sulphuretted hydrogen. The retort is connected with a receiver, in which is placed a little water, the object of which is to collect a little chloride of arsenic that volatilizes during the process. The retort is heated by a bath of chloride of calcium until the mass acquires the consistence of paste, when it is allowed to cool. The mass is then mixed with about twice its weight of strong alcohol, and after some time the undissolved portion is collected on a filter, and washed with alcohol. The alcoholic liquid and the washings are, lastly, introduced into a retort, and the alcohol is distilled off; the residue in the retort is mixed with the acid liquor which distilled into the receiver during the first distillation, and the mixture is exposed to sulphuretted hydrogen.

3. The mode of preparing the material proposed by M. Fresenius, in a recent paper on testing for arsenic†, is as follows: — The substance for examination, reduced to small pieces, which are carefully intermixed, is placed in a large porcelain bason, and mixed with about an equal quantity of concentrated hydrochloric acid (free from arsenic), and enough water to give the mixture the consistence of thin paste. The bason is heated by a water-bath, and chlorate of potash is

* Berzelius's *Rapport Annuel*, 1844, p. 136.

† Memoirs and Proceedings of the Chemical Society, Part IX. p. 130.

introduced by small quantities at a time (half a drachm every five minutes), until the mixture appears bright yellow, homogeneous, and quite liquid: about two drachms more of chlorate of potash are then added, and the bason is removed from the water-bath, and allowed to cool. When cold, the liquid is passed through a filter, the residue in the filter is washed with hot water until the filtered liquid is no longer acid to test-paper, and the whole of the filtered liquid is concentrated by evaporation (by means of a water-bath) to about a pint. A saturated aqueous solution of sulphurous acid is then mixed with the acid liquid, until the smell of sulphurous acid is strongly perceptible, and the mixture is again heated for about an hour, in order to expel the excess of sulphurous acid. The liquid is then ready for exposure to sulphuretted hydrogen.

(B). *Precipitation of the sulphuret of arsenic.* — The liquid is next exposed for several hours to a slow stream of sulphuretted hydrogen gas, passed first of all through a little water; after which the liquid is moderately heated in a loosely covered vessel, until the odour of sulphuretted hydrogen has disappeared. The precipitated sulphuret of arsenic is now collected by passing the liquid through a small paper filter. After the sulphuret has been washed, but while still moist, it is dissolved in caustic ammonia, and the filtered ammoniacal solution is evaporated to dryness in a porcelain capsule. The dry residue is then ready for the next operation.

(C). *Reduction of the sulphuret of arsenic.* — The manner of obtaining metallic arsenic from sulphuret of arsenic has already been described at page 108. A more minute account of the various precautions to be adopted may be found in the paper of M. Fresenius, before referred to, in the *Memoirs and Proceedings of the Chemical Society*, p. 132. In judicial investigations, the reduction of the sulphuret should always be effected by means of the mixture of carbonate of potash and cyanide of potassium, instead of black flux.

The mode of testing for arsenic last described is considered the safest and most certain in its indications, but is not the most delicate. The processes of M. Reinsch and Mr. Marsh are both extremely delicate, but are subject to certain inconveniences, particularly that of Mr. Marsh, as has been already pointed out. The principal objection to M. Reinsch's process is, that its indications are impeded or prevented by the presence of nitrates, and salts of mercury, and some other metals. For facility of application, however, it is decidedly preferable to either of the other two methods, and in point of delicacy, it is not inferior to the process of Mr. Marsh.

2. *Mercury.*

The mixture suspected to contain mercury is to be evaporated almost to dryness, and the organic matter destroyed by boiling the residue with aqua regia. The liquid is evaporated nearly to dryness, to expel most of the excess of acid, diluted with water, and filtered. The solution thus obtained may either, 1°, be treated with sulphuretted hydrogen, and the precipitated sulphuret subsequently reduced by being heated, in a small glass tube, with carbonate of soda; or, 2°, the solution may be mixed with protochloride of tin, and the precipitated metallic mercury collected, dried, and sublimed in a dry glass tube (p. 94.); or, 3°, the liquid may be subjected to galvanic action, the positive pole being a plate of gold or a gold wire: the gold becomes whitened if mercury is present; and when washed, dried, and heated in a dry glass tube, the mercury rises in vapour and condenses in globules on the sides of the tube. (page 92.)

3. *Antimony.*

When introduced as tartar emetic, antimony may exist in organic fluids, either in solution, or it may be rendered insoluble by combining with organic compounds. A mixture of tartaric and muriatic acids is first added to the suspected mixture, the former to dissolve out oxide of antimony from its insoluble compounds, the latter to coagulate various

animal principles which may be present. Filter and transmit sulphuretted hydrogen gas through the solution; an *orange-coloured* precipitate of sulphuret of antimony will be formed, if that metal is present. Collect the precipitate, dry, and heat it in a small capsule with strong hydrochloric acid; it is then dissolved, with evolution of sulphuretted hydrogen: evaporate off nearly all the excess of hydrochloric acid, and pour the liquid residue into pure water, on which a white precipitate of oxichloride of antimony will be produced. (p. 85.)

Another mode of preparing the organic material to receive sulphuretted hydrogen, is the following: — The substance is boiled with concentrated sulphuric acid, and the mixture is cooled immediately it becomes liquid: nitrate of soda is then added, and the carbonization of the mass is continued. The dry carbonaceous mass is digested in a solution of tartaric acid, and the solution thus obtained is exposed to sulphuretted hydrogen. (MM. Danger and Flandin.)

In cases of poisoning by a compound of antimony, that metal should especially be sought for in the vomitted matters, and in the contents of the stomach and intestines.

4. *Copper.*

This metal, like the preceding, may be present in an organic mixture in two states; in solution, and in a state of combination with organic principles, forming insoluble compounds. As acetic acid dissolves out the oxide of copper from most of these organic compounds, the mixture, after being boiled, should be treated with that acid, diluted and filtered. Sulphuretted hydrogen gas is now passed through the solution, when, if copper is present, a black or brown precipitate of the sulphuret is formed, which, after boiling the liquid, is to be washed by affusion and subsidence. The precipitate is then collected in a porcelain capsule, heated to redness with access of air, to destroy any organic matter with which it may be mixed, and treated with nitric acid to dissolve the copper. The solution thus obtained may be tested with ammonia, or any other characteristic test of copper.

(p. 88.) If necessary to examine the portions of the suspected mixture insoluble in acetic acid, the matter should be well dried, and heated to redness in a porcelain crucible, by which most of the copper will be reduced to the metallic state. The residue, treated with nitric acid, affords a solution to which the usual tests for copper may be applied.

5. *Lead.*

Add a little nitric acid to the suspected mixture before filtration, to dissolve the compounds of oxide of lead and organic matters, and transmit sulphuretted hydrogen gas through the filtered liquid. Boil the liquid and collect the precipitate on a filter. To prove the existence of lead in the precipitate, digest it in moderately strong nitric acid, with the assistance of a very gentle heat, by which the lead will be dissolved, while almost all the sulphur remains unacted on. If strong nitric acid is employed, the sulphur will be converted into sulphuric acid, and the insoluble sulphate of lead formed. The acid solution of nitrate of lead must be poured off from the sulphur, evaporated to dryness, and redissolved in water. This solution can then be examined by chromate of potash, or any other test for lead. (p. 91.)

Instead of digesting the sulphuret of lead in nitric acid, it may be examined before the blowpipe, by heating with soda on charcoal, when it gives a globule of metal easily recognised as lead, by its softness, ready fusibility, and the peculiar lustre of its freshly cut surface.

6. *Nitric acid.*

Neutralize the liquid for examination with potash, filter, and evaporate to obtain crystals of nitre. To the salt thus obtained, the test of protosulphate of iron and sulphuric acid may be applied (page 155.); or the crystals may be mixed with sulphuric acid and copper filings, when ruddy fumes of peroxide of nitrogen are perceived arising from the nitric oxide evolved. If much organic matter is present, the nitrate of potash will not crystallize; in which case the dry residue of

evaporation is redissolved, and a solution of acetate of silver added, which not only removes organic matters, but also decomposes the chloride of sodium present in almost all organic liquids, and which would interfere when the crystallized salt is treated with sulphuric acid, by producing free chlorine. After precipitation by acetate of silver, filter, and evaporate to obtain crystals. (Christison.)

7. *Sulphuric acid.*

Although introduced in the state of oil of vitriol, sulphuric acid may soon exist in the form of a neutral sulphate, from coming in contact with bases or carbonates, or from the gradual formation of ammonia through decomposition of the animal matters. This acid, therefore, when suspected, must be looked for as well in the free as in the combined state. The existence of a free acid in considerable quantity having been ascertained by blue litmus paper, if the liquid does not give the usual appearance presented by sulphuric acid with a salt of barytes (page 120.), in consequence of the presence of organic matters, it must be distilled to dryness in a proper retort and receiver, the heat being increased to dull redness towards the close. The receiver should contain a dilute solution of ammonia, to arrest all the sulphurous acid which is formed by the action of the organic substances on sulphuric acid. On treating the distilled product with aqua regia, the sulphurous acid is again converted into sulphuric acid, the presence of which is then easily ascertained by chloride of barium.

If the sulphuric acid is in a state of combination with bases, the liquid suspected to contain it may be filtered, and the ordinary tests applied. In examining organic mixtures for sulphuric acid, it is always necessary to discriminate between the small quantity naturally contained in these mixtures, and the large excess which is found when sulphuric acid is really administered with a criminal intention. To do this satisfactorily, a quantitative analysis must generally be had recourse to.

8. *Hydrochloric acid.*

Nitrate of silver, the ordinary test for hydrochloric acid, cannot be applied to the contents of the stomach, from the constant presence of chlorides, as well as of organic matters which precipitate salts of silver. The mixture suspected to contain hydrochloric acid must be cautiously distilled to dryness (not merely to a syrup), in a chloride of calcium bath, composed of about equal parts of that salt and water. The test of nitrate of silver with nitric acid (page 136.) is then applied to the product of the distillation. If the subject of examination is the contents of the stomach, and a mere trace only is detected, no conclusion as to poisoning can be drawn, as this may have actually existed as an ingredient of the gastric juice.

To get rid of the organic matter which impedes the distillation of the acid, Orfila recommends the addition of a concentrated infusion of galls to the contents of the stomach, until no further precipitate is produced. The precipitate is allowed to subside, and the reddish-yellow supernatant liquid is carefully distilled at a moderate heat until the residue is nearly dry, the receiver being kept very cold.

9. *Oxalic acid.*

The mixture suspected to contain this acid is first filtered and mixed with carbonate of potash. The oxalic acid is then precipitated by a solution of acetate of lead; the precipitate (partly oxalate of lead) is collected on a filter, washed, diffused in water, and decomposed by sulphuretted hydrogen: sulphuret of lead and free oxalic acid are formed. The mixture is then filtered, heated to expel sulphuretted hydrogen, and a salt of lime applied as a test for oxalic acid, as directed at page 126.

If lime or magnesia has been administered as an antidote, this process must be somewhat modified. The suspected mixture is allowed to stand some time to permit the insoluble oxalate to subside, and the supernatant liquid decanted.

The insoluble residue is now boiled with a solution of carbonate of potash, and filtered. By this operation there are formed a carbonate of the earth and oxalate of potash. Add to the solution a slight excess of nitric acid, filter, render the liquid alkaline by carbonate of potash, and filter again. The object of these operations is to get rid of animal matter, some portion being removed at each step. The alkaline solution of oxalate of potash is now mixed with acetate of lead, and the precipitated oxalate treated as above by sulphuretted hydrogen.

10. *Hydrocyanic acid.*

If the organic mixture is of such a nature as to prevent the detection of this acid by its usual tests, recourse must be had to distillation. The mixture is first filtered, mixed with sulphuric acid, to combine with all the ammonia which may have been produced by the decomposition of organic matters, and then distilled in a water-bath until one eighth has been collected. To this product the tests of nitrate of silver and of potash and protosulphate of iron (page 143.) are applied.

11. *Alcohol.*

According to Dr. Christison, alcohol may be detected in the contents of the stomachs of persons who have died from the excessive use of spirits several weeks after death. To separate the alcohol, the contents of the stomach are mixed with a quantity of carbonate of potash, and carefully distilled; the distilled product is mixed with sulphuric acid to combine with ammonia, and redistilled until one fifth has passed over. The product thus obtained is agitated with dry carbonate of potash, on which alcohol of about the strength of rectified spirit rises to the surface.

CHAPTER X.

QUALITATIVE ANALYSIS OF URINE, AND DISCRIMINATION
OF URINARY CALCULI.

SECTION I.

QUALITATIVE ANALYSIS OF URINE.

URINE should be submitted to examination soon after it is voided, as it is subject to alteration in its characters by exposure to the air. The action of the urine on delicate test paper may first be observed: healthy urine is always slightly acid to test paper. The specific gravity of the urine should next be determined. That of healthy urine is from 1015 to 1025: when the specific gravity is 1030, or higher, the presence of sugar or of an excess of urea may be suspected.

The substances to be sought for are the following: urea; uric acid; urate of ammonia; mucus; phosphates of lime, magnesia, and alkalies; alkaline sulphates and chlorides; albumen, and sugar.

1. *Urea*.—To detect urea, evaporate some of the urine to one eighth part of its original bulk, and add half its reduced volume of nitric acid. Crystals of nitrate of urea are deposited either immediately or on standing a short time. If the urine is albuminous, it may be evaporated to dryness by a water-bath, the dry residue digested in boiling alcohol, and the alcoholic liquid evaporated to dryness. This residue is redissolved in a little water, and the solution tested with nitric acid as above. If the urine contains sugar, in order to test it for urea it is mixed with a little yeast and kept slightly warm; when all fermentation has ceased, the liquid is evaporated to

dryness, and the residue treated with alcohol, &c., as in the case of albuminous urine.

2. *Uric acid and urate of ammonia.* — When half a pint of urine is mixed with a few drops of nitric acid, and the mixture allowed to stand for several hours, uric acid (proceeding from the decomposition of urate of ammonia) is deposited on the sides of the vessel in minute crystals. If these crystals are collected, dissolved in a small quantity of nitric acid, and the solution evaporated to dryness, the addition of ammonia to the residue develops a purple colour, owing to the formation of murexid.

Uric acid requires 10,000 parts of cold water for its solution: it is soluble in solution of potash without the disengagement of ammonia in the cold, and is reprecipitated from the alkaline solution by the addition of hydrochloric acid.

Urate of ammonia is soluble in about 500 parts of cold water, and much more freely in boiling water. It dissolves in solution of potash with evolution of ammonia. It is entirely dissipated by exposure to a red heat, if free from the urates of soda and lime. Urate of ammonia is precipitated when urine is evaporated over a surface of sulphuric acid under the receiver of an air-pump.

3. *Mucus.*—Soon after the urine is voided, mucus, if present, is deposited as a light cloud, soluble in nitric acid, acetic acid, and potash, but not in sulphuric acid. It is precipitated from its solution in an acid by yellow prussiate of potash. An infusion of gall-nuts precipitates mucus from urine.

4. *Fixed alkaline and earthy salts.*—The white ash obtained by incinerating at a moderate heat the residue of the evaporation of urine may contain phosphates of soda, lime, and magnesia, sulphates of potash and soda, common salt, and alkaline and earthy carbonates, proceeding from the decomposition of lactates, oxalates, and urates. By the application of water, the *alkaline salts* are separated from the *earthy salts*. The aqueous solution is tested in the usual way for *chlorine*, *sulphuric acid*, and *phosphoric acid*. The portion of the ash insoluble in water may be dissolved in a little hydrochloric acid, and a part of the solution tested for *phos-*

phoric acid by the test described at page 127.; the remainder of the hydrochloric acid solution is nearly neutralized with ammonia, and tested first for *lime* with oxalate of ammonia, and after filtration, for *magnesia*, by excess of ammonia, which should produce a precipitate of ammonio-phosphate of magnesia.

When ammonia is added to urine, the whole of the *earthy phosphates* is precipitated. If such a mixture, after filtration, produces a precipitate with lime-water, *alkaline phosphates* are present.

When oxalate of potash is added to urine, *lime* is precipitated as oxalate. If ammonia is afterwards added, *magnesia* is precipitated as ammonio-phosphate.

When urine which contains an excess of earthy phosphates is boiled, it becomes turbid: if the turbidity disappears on the addition of a few drops of nitric acid, and is not reproduced by a larger quantity of nitric acid, it proceeds from earthy phosphates, and not from albumen.

Oxalate of lime is sometimes formed as a crystalline deposit from urine. It is recognised by its insolubility in acetic acid, and in becoming converted by gentle ignition into carbonate of lime, which effervesces with acids. (page 126.)

5. *Sugar*.—A very convenient and satisfactory test for the presence of sugar in urine is the following, proposed by M. Trommer. To the suspected urine contained in a large test-tube, add first a few drops of a solution of sulphate of copper, and afterwards, a decided excess of solution of caustic potash. The hydrated oxide of copper at first precipitated by the alkali redissolves in the excess of alkali, either partially or entirely, if sugar is present, forming a purplish-blue liquid similar to the ammoniacal solution of oxide of copper. On applying a gentle heat to the liquid, hydrated suboxide of copper is precipitated as a copious yellowish-brown powder. A little oxide of copper may be dissolved by the excess of alkali, although sugar is absent; but, in that case, the liquid does not afford the yellowish precipitate of hydrated suboxide of copper on being warmed. This test for sugar in urine is not only the most convenient that is known, but is highly characteristic and delicate.

The presence of sugar in urine may also be discovered by adding a little yeast, and keeping the mixture moderately warm. The vinous fermentation soon ensues if the urine contains sugar. The quantity of sugar may be roughly estimated by ascertaining the amount of carbonic acid disengaged: one cubic inch of gas corresponds to nearly one grain of sugar.

6. *Albumen*.—Urine which contains albumen is usually muddy and dull. When urine which contains albumen is boiled, the albumen is precipitated as an opaque white cloud, which is distinguished from the similar deposit of earthy phosphates by the application of nitric acid. A small quantity of nitric acid dissolves both albumen and the phosphates, but the former is reprecipitated by a further addition of nitric acid, while the phosphates remain in solution.

SECTION II.

DISCRIMINATION (BY CHEMICAL TESTS) OF URINARY CALCULI, CONSISTING OF A SINGLE DEPOSIT, OR OF ALTERNATING CALCULI.

1. *Bone-earth calculus*.—This calculus is insoluble in potash and in acetic acid, but soluble in dilute nitric and hydrochloric acids. Before the blowpipe it first becomes black, and afterwards white: it is fused with difficulty.

2. *Ammonio-magnesian phosphate*.—It does not dissolve, but evolves ammonia, when digested in solution of potash. It is soluble in cold acetic and dilute nitric acids, and is reprecipitated by ammonia. It gives off ammonia at 212° , and melts into a white pearl before the blowpipe.

3. *Fusible calculus*.—A portion of this calculus is dissolved by acetic acid, and the remainder by hydrochloric acid. It readily fuses to a pearly bead before the blowpipe.

4. *Uric acid calculus*.—It is readily soluble in potash, and

is reprecipitated by acids. In strong nitric acid it dissolves with effervescence, the solution leaving, when evaporated to dryness, a residue, which on being treated with an excess of ammonia becomes of a purple-red colour. Uric acid is nearly insoluble in hydrochloric acid. Before the blowpipe it evolves an ammoniacal odour and blackens, leaving a minute portion of a white ash, which possesses an alkaline reaction.

5. *Urate of ammonia calculus*.—It is soluble in potash with evolution of ammonia. It is soluble in alkaline carbonates, while uric acid is not. With nitric acid it behaves as uric acid does. It usually decrepitates before the blowpipe.

6. *Cystic oxide calculus*.—This calculus is soluble in alkalis and in the carbonates of the fixed alkalis, giving a solution which is decomposed by heat, ammonia being first evolved, and after some time a combustible gas, smelling like bisulphuret of carbon. It is soluble in phosphoric, hydrochloric, sulphuric, nitric, and oxalic acids; and insoluble in water, alcohol, bicarbonate of ammonia, and tartaric, citric, and acetic acids. Before the blowpipe it exhales a peculiar fœtid odour.

7. *Xanthic oxide calculus*.—It is completely dissolved by potash, and is reprecipitated by carbonic acid, as a white powder, which becomes on drying a pale yellow agglutinated mass, possessing a waxy appearance. It is soluble in nitric acid with effervescence. When that solution is evaporated to dryness, and the residue treated with ammonia, no red colour is developed, as with uric acid. This calculus is very slightly soluble in hot water and in hydrochloric and oxalic acids. Concentrated sulphuric acid dissolves it, forming a yellow solution.

8. *Oxalate of lime calculus*.—This calculus is insoluble in potash: it is decomposed by digestion in carbonate of potash, with formation of carbonate of lime and oxalate of potash. It is insoluble in acetic acid, but soluble in hydrochloric and nitric acids. When heated to dull redness, it is converted into carbonate of lime, which dissolves in acids with effervescence. If heated before the blowpipe, it is reduced to quick-lime,

which, when moistened, produces an alkaline reaction on test paper.

9. *Carbonate of lime calculus*.—It dissolves with effervescence in dilute acids, affording a solution which gives a precipitate with oxalate of ammonia.

10. *Calculi containing silica* leave, after calcination before the blowpipe, an infusible ash (principally silica), which dissolves in a melted bead of carbonate of soda with effervescence, producing a vitreous pearl, more or less limpid.

PART IV.

QUANTITATIVE ANALYSIS.

QUANTITATIVE ANALYSIS.

PRELIMINARY OBSERVATIONS.

THE portion of material employed in a Quantitative Analysis should not in general exceed thirty grains: from twenty to twenty-five grains of an inorganic body is the most convenient quantity, except in those cases in which a substance existing in minute proportion is to be determined, when more may be used. When a larger amount is operated on, the chances of error in the analysis are seldom reduced; while, from the greater quantities of precipitates to be filtered and washed, and of liquids to be evaporated, a much longer time is necessary for the execution of the analysis. If the substance to be analyzed is solid and pulverizable, it must be reduced to a fine power, and cautiously dried, to get rid of all hygrometric moisture without expelling any of its chemically combined water. A temperature of from 100° to 150° Fahr. is quite sufficient to effect this; but if the body parts with its combined water at that degree of heat, it is then necessary to dry it at common temperatures, by exposure to a surface of oil of vitriol in a close vessel. The oil of vitriol is most conveniently contained in a shallow bason, across the top of which are placed wires to support a piece of bibulous paper, on which the substance to be dried is strewed. The bason is placed on a level surface, and covered with a bell jar, having a ground bottom, to which a little grease is applied in order to render the jar air-tight; or, the bason may be placed under the receiver of an air-pump, in which a vacuum is maintained. Six or eight hours' exposure is generally sufficient. To prevent the absorption of any water during the weighing, the substance should be weighed in a tube about two inches in length and a quarter of an inch in diameter, transferred directly to the vessel in which it is to be dissolved, and the

weight of the empty tube with its adhering particles ascertained and deducted from the entire weight of the tube and substance. If the substance for analysis is a liquid, it may be weighed in a specific-gravity bottle, whose weight when empty has been previously ascertained; the liquid is poured out into a convenient vessel, and the bottle washed out several times with distilled water, the washings being added to the original liquid.

It has already been stated that a substance is generally obtained in a fit state for weighing by precipitation from a state of solution. (See page 8.) Particular processes will now be described, which are practised in the quantitative estimation of bodies, supposing those bodies or their compounds to exist in a state of purity, with the various methods of separating substances from one another in a state of mixture, for the purpose of their quantitative determination; commencing with the alkalies and earths, and proceeding to the metals proper and non-metallic bodies; those mixtures only being considered which occur in nature or are likely to be presented for examination. I have pursued as far as possible the plan adopted by Rose, in his valuable "*Handbuch der Analytischen Chemie*," of treating, under each substance, of the mode of separating it from those bodies which have been previously considered; so that a method of separating any two substances being required, the process, if given, will generally be found under the last-mentioned of the two bodies in question.

In quantitative as in qualitative analysis, advantage is taken of certain similarities in the properties of bodies, which permit of their classification into groups, separable from each other by a single agent: thus sulphuretted hydrogen removes one class of metals proper from a solution, and hydrosulphate of ammonia another class, leaving earths and alkalies, the former of which may be precipitated by a fixed alkaline carbonate.

CHAPTER I.

ALKALIES AND THEIR METALLIC BASES.

SECTION I.

POTASSIUM.

If the potash to be weighed exists either as sulphate or nitrate, or as chloride of potassium, the salts are weighed as such, if pure, and the quantity of base contained in them is calculated.*

If the potash is in a state of solution as *neutral sulphate*, evaporate the liquid to dryness in a platinum or porcelain capsule; transfer the residue carefully to a weighed platinum crucible, ignite the salt with the cover of the crucible on, to prevent loss by decrepitation, and weigh what remains. If an excess of sulphuric acid existed in the solution, the bisulphate of potash will be formed, which must be converted into the neutral sulphate before weighing. This is done by placing a piece of dry carbonate of ammonia in the crucible, when heated nearly to redness, and afterwards heating more strongly. The excess of sulphuric acid then volatilizes as sulphate of ammonia, neutral sulphate of potash remaining in a state fit to be weighed.

When the potash exists as *nitrate*, the solution is evaporated to dryness in a weighed platinum capsule, and kept at a temperature of 212° until the weight of the nitrate becomes constant.

If as *chloride of potassium*, the only particular precaution to be observed is, that this salt must not be heated above a dull-red heat, as it is volatile at somewhat higher temperatures.

If united to the weaker *volatile acids*, the salt of potash must be converted into the sulphate, or into chloride of

* Tables for calculations in analysis are given in the Appendix.

of potassium, by the addition of sulphuric or hydrochloric acid; the solution is evaporated to dryness, and the residue ignited with the precautions above mentioned.

When in combination with an acid which when free is soluble in alcohol, potash is sometimes estimated as the double chloride of platinum and potassium. The solution is evaporated to a small bulk, mixed with solution of chloride of platinum, and evaporated nearly to dryness. When treated with alcohol, the residue dissolves, with the exception of the double chloride of platinum and potassium, which is collected on a weighed filter (page 15.), washed with alcohol, dried and weighed on the filter. From the weight of the double salt that of the potassium it contains may be calculated. (See the Tables in the Appendix.)

If it is known with certainty that all the potash present in a solution is in the state of neutral sulphate, or as chloride of potassium, and that no sulphuric acid or chlorine is present, except in combination with potash (or potassium), then the amount of potash (or potassium) is determined indirectly by estimating the sulphuric acid, or chlorine, by processes elsewhere described: 40 parts of sulphuric acid, and 35·47 parts of chlorine, indicate 47·3 parts of potash, or 39·2 parts of potassium. The same observations apply to the estimation of soda: 40 parts of sulphuric acid, and 35·47 parts of chlorine, indicate 31·3 parts of soda, or 23·3 parts of sodium.

SECTION II.

SODIUM.

Soda may be weighed either in the state of sulphate or soda, or chloride of sodium; the same precautions being observed in the separation and ignition of these salts as with the corresponding compounds of potassium. (See the last paragraph of the previous section on the estimation of potash.)

Separation of potash from soda.—One process for the separation of these alkalis is founded on the solubility of the chloride of platinum and sodium, and the insolubility of the corresponding chloride of platinum and potassium. Both alkalis are converted into chlorides, ignited, and weighed. They are then redissolved in water, and mixed with 3·7 times their weight of crystallized chloride of platinum and sodium, which precipitates the chloride of platinum and potassium. The precipitate is collected and weighed in the manner described under potassium, and from its amount, that of the chloride of potassium is calculated. The weight of the latter deducted from the weight of the mixed chlorides, gives that of the chloride of sodium.

If hyperchloric (perchloric) acid is added to a mixture of potash and soda salts, it precipitates potash, but not soda. The mixture is evaporated nearly to dryness, and the residue treated with alcohol, in which hyperchlorate of potash is quite insoluble. This salt is collected on a filter, dried, and heated carefully to dull redness, when it leaves chloride of potassium, which may be weighed, and the corresponding amount of potassium, or of potash or salt of potash, calculated. The weight of the mixed salt of soda and potash being known, the loss expresses the quantity of the soda salt.

When existing as sulphates (into which most salts of the alkalis may be converted by the addition of sulphuric acid), add to the mixture an excess of a solution of hyperchlorate of barytes; collect the precipitate, which consists of hyperchlorate of potash and sulphate of barytes, on a filter, and wash it with hot water to dissolve out the former salt. If the sulphates did not contain excess of acid, the weight of the sulphate of barytes may be ascertained, and from it that of the sulphuric acid calculated. Evaporate the filtered liquid to dryness, and treat the residue with alcohol, by which hyperchlorate of soda and the excess of hyperchlorate of barytes are dissolved, and an insoluble residue of hyperchlorate of potash remains, which is filtered, washed with alcohol, dried, ignited, and weighed as chloride of po-

tassium. The filtered alcoholic solution, containing hyperchlorates of soda and barytes, is evaporated to dryness, the salts are redissolved in water, and sulphuric acid is added to precipitate barytes. Filter and evaporate the solution, which now contains sulphate of soda, to dryness: ignite the residue with a little carbonate of ammonia, and weigh it as neutral sulphate of soda. If the alkalies exist as chlorides, a similar process to the last is followed, hyperchlorate of silver being substituted for hyperchlorate of barytes, and hydrochloric acid for sulphuric acid. Chloride of silver is then formed in the steps in which sulphate of barytes would otherwise be obtained.

These direct methods of analyzing a mixture of a potash salt with a soda salt are tedious and complex, and do not afford very accurate results. An indirect but more satisfactory process has been devised, founded on the difference which exists between the combining numbers of potassium and sodium. This process is applicable to the sulphates of potash and soda, and to the chlorides of potassium and sodium: if other salts of potash and soda are present, they should be converted into neutral sulphates or chlorides. If the two alkalies are in the state of neutral sulphates, the solution is evaporated to dryness, the residue is weighed with great nicety, when perfectly dry, and redissolved in water. The *sulphuric acid* in the solution of the mixed sulphates is then accurately determined by a salt of barytes, in the usual way, as described under the subject of sulphuric acid. From the weight of the mixed dry sulphates, and the quantity of sulphate of barytes they produce, the relative quantities of potash and soda required are obtained by calculation.

1 part of neutral *sulphate of potash* produces 1·31818 of *sulphate of barytes*, and

1 part of neutral *sulphate of soda* produces 1·61111 of *sulphate of barytes*.

The number of grains of the material used is multiplied by 1·31818; the product is subtracted from the number of grains of sulphate of barytes obtained by experiment; the remainder, divided by 0·29293, gives the quantity required

of sulphate of soda, which, when deducted from the amount of material used, of course leaves the quantity of sulphate of potash required. Suppose 20 grains of the mixed sulphates to give 28.45 grains of sulphate of barytes, then the calculations are as follow: $20 \times 1.318 = 26.36$; $26.36 \quad 28.45$
 $= 2.09$; $2.09 \div 0.29293 = 7.13$. Therefore 7.13 is the number of grains of sulphate of soda in 20 grains of the mixed sulphates; leaving 12.87 grains of sulphate of potash.

If the two alkalis are in the state of chlorides, instead of sulphates, the process for their estimation is precisely analogous. The total weight of the mixed chlorides is first obtained with great accuracy, and afterwards their amount of chlorine is determined by nitrate of silver in the ordinary manner:—

1 part of *chloride of potassium* produces 1.894 of *chloride of silver*, and

1 part of *chloride of sodium* produces 2.400 of *chloride of silver*.

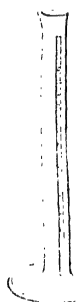
The calculation, therefore, is as follows: the number of grains used of the dry chlorides is multiplied by 1.894; the product is subtracted from the number of grains of chloride of silver obtained by experiment; the remainder divided by 0.506 gives the quantity of chloride of sodium required, which, when subtracted from the number of grains of material employed, gives the amount of chloride of potassium.

ALKALIMETRY.

The branch of chemical analysis termed Alkalimetry has for its object the determination of the value of the carbonates of potash and soda met with in commerce, by making an estimation of their proportion of available alkali. The available alkali is that which exists in the free or caustic state, and that which exists as carbonate. Two simple processes for obtaining this have been contrived, by which results of sufficient accuracy for all ordinary purposes may be obtained with ease, after a very little experience.

I. In one of these methods, the experiment consists in finding what quantity of an acid is required to destroy the alkaline reaction of a known weight of the specimen to be tested: in examining a soda ash which contains none other than the usual impurities, common salt and sulphate of soda, the quantity of acid required for the neutralization is of course exactly equivalent to the quantity of soda present in the free state and as carbonate.

In this operation, a tube measure called an alkalimeter is employed (fig. 19.), about fourteen inches in height,



and five eighths of an inch in diameter, mounted on a foot, and capable of holding, when full, a little more than 1000 grains of water. It is graduated up to this amount into one hundred divisions, numbered from the top downwards; each division, therefore, contains ten grains of water.

The acid employed is sulphuric, made of such a strength that a single measure of the alkalimeter (ten grains measure of distilled water) is sufficient to neutralize exactly one grain of pure soda. Acid of this strength is obtained in the following manner: 170.6 grains of pure carbonate soda (obtained by heating the bicarbonate to dull redness in a platinum or porcelain crucible) are dissolved in four or five ounces of hot water. This quantity contains exactly 100 grains of pure soda. A quantity, say a pint, of a dilute acid is prepared by mixing one part of oil of vitriol with ten of water by measure, with which the alkalimeter is filled up to 0 (1000 grains measure of water), and poured from this very gradually into the solution of carbonate of soda above mentioned, until it has destroyed the alkaline reaction of the latter on test paper, and the mixture has become very feebly acid. The quantity of acid which has been required to produce this effect is accurately observed. Supposing it to be 90 measures, that quantity is of course equivalent to 100 grains of soda; but an acid is wanted, of which 100 measures, instead of 90, are required to neutralize the soda: to procure this we have simply to add to 90 volumes of the acid, 10 volumes of water,

so that the same amount of real acid which was before contained in 90 shall now be contained in 100 parts. For this, any vessel of sufficient capacity, divided accurately into 100 equal parts, will suffice. Such is the method of preparing the *test acid*, of which 1 alkalimeter measure (10 grains of water) is equivalent to 1 grain of pure soda: 22 measures should neutralize 100 grains of crystallized carbonate of soda, and $58\frac{1}{2}$ measures, 100 grains of anhydrous carbonate of soda.

In performing an actual analysis, 100 grains of the soda salt to be tested are weighed, dissolved in about three ounces of hot water, filtered if any carbonate of lime remains undissolved, and neutralized with the test acid poured from the alkalimeter. The number of measures required represents the amount of soda per cent. in the specimen. If 50 grains of the soda-ash are operated on instead of 100, the number of measures must of course be doubled to obtain the percentage of soda. The test paper employed in alkalimetry should be exceedingly delicate; and a distinction must be made between the purplish-red tint which carbonic acid produces, and the distinct reddening produced by sulphuric acid, which should be the indication to guide the operator. The slight reddening which carbonic acid produces may be discharged by the application of a gentle heat.

If the only impurities contained in the soda-ash to be tested are chloride of sodium, sulphate of soda, and insoluble matters, the process just described may afford results of sufficient accuracy; but frequently other bodies are present which interfere with this process by neutralizing a portion of the test acid, such as sulphuret of sodium, and sulphite and hyposulphite of soda, which are liable to occasion a considerable error by taking up the sulphuric acid. One method of avoiding this source of fallacy consists in mixing the solution of the ash with chlorate of potash, evaporating to dryness, and heating the residue to redness; the sulphuret, sulphite, and hyposulphite are thereby converted into the sulphate of soda, which does not interfere in the process. A more convenient method of avoiding error from this source may be

adopted when the soda-ash is tested by another alkalimetric process, to be noticed immediately.

The same test acid used for soda may also be employed in analyzing the carbonates of potash; but as the equivalent of potash is higher than that of soda, the number of measures poured from the alkalimeter cannot represent the per centage of this alkali, as it does of soda. A simple calculation, however, reduces the numbers for soda to those for potash; their respective equivalents being very nearly as 2 to 3, the number of measures necessary to saturate 100 grains of the specimen, multiplied by 3 and divided by 2, gives the per centage of potash required.

II. In the other alkalimetric process above alluded to, the proportion of available alkali is determined by observing the amount of carbonic acid gas disengaged on the neutralization of the *carbonate*, which amount is exactly proportional to the quantity of pure alkali in the carbonate decomposed. This process is, therefore, of no value when the soda-ash contains either caustic soda or bicarbonate of soda. The mode of conducting this operation is described under the head of carbon (*Analysis of Carbonates*).

If all the available alkali is in the state of neutral carbonate, and no sulphite or hyposulphite of soda or sulphuret of sodium is present to occasion an evolution of sulphurous acid or sulphuretted hydrogen, then the value of the soda-ash may be calculated from the loss in the weight of the flask used in this operation, at the close of the experiment: 22 parts (1 eq.) of the disengaged carbonic acid indicate 31.3 parts (1 eq.) of soda; 1 part of carbonic acid indicates 1.4227 parts of soda.

The ingredients of soda-ash which would affect the results obtained by this process are carbonate of lime, sulphite and hyposulphite of soda, sulphuret of sodium, caustic soda, and bicarbonate of soda.

The inconvenience which arises from the presence of carbonate of lime, may be surmounted by dissolving the soda-ash in water and filtering the solution; but the filtered liquid

requires to be concentrated by evaporation to a very small bulk, proportional to the size of the flask. This operation, however, rarely needs to be practised in testing soda-ash for commercial purposes.

The presence of sulphite or hyposulphite of soda or sulphuret of sodium may be detected by adding some of the soda-ash to dilute sulphuric acid, coloured reddish-yellow with bichromate of potash, the alkali not being added in sufficient quantity to saturate the acid. If the above salts are present, the reddish-yellow colour is changed to green, owing to the deoxidation of the chromic acid and formation of oxide of chromium. Soda-ash which contains sulphuret of sodium gives a black precipitate with a solution of acetate of lead, and disengages the odour of hydrosulphate of ammonia when moistened with a solution of common carbonate of ammonia. To avoid the evolution of sulphurous acid or sulphuretted hydrogen during the operation, MM. Fresenius and Will recommend the addition to the soda-ash of a small quantity of yellow chromate of potash, the chromic acid of which serves to oxidize the sulphurous acid into sulphuric, and the hydrogen of the sulphuretted hydrogen into water, with separation of sulphur. As soda-ash is seldom or never altogether free from one of these impurities, the yellow chromate may be always added in this mode of testing, and the trouble of first ascertaining the presence of the sulphite, &c., by a preliminary experiment be avoided.

A convenient method of determining on the presence or absence of caustic soda in the carbonate of commerce consists in adding an excess of perfectly neutral chloride of barium to the soda-ash, treating the mixture with hot water and filtering; if the filtered liquid produces an alkaline reaction on test paper, the presence of caustic soda may be inferred. Sulphuret of sodium would behave with this test in the same manner as caustic soda; but the sulphuret is never found unaccompanied by the caustic alkali. Before a specimen of soda-ash containing caustic soda can be tested for its alkali by the process last described, the caustic soda must be converted into neutral carbonate. To effect this, the weighed sample

may be rubbed up with from one fourth to one third of its weight of powdered carbonate of ammonia, and three or four parts of siliceous sand; the mixture is placed in a porcelain capsule, thoroughly wetted with water, and then heated until the whole of the water and carbonate of ammonia is expelled. (MM. Fresenius and Will.) In this operation the caustic soda unites with the carbonic acid of the ammoniacal salt, and free ammonia is disengaged. When the odour of ammonia is no longer perceived, the mass is transferred to the flask and decomposed in the ordinary manner. The principal use of the sand is to prevent the mass from caking. When the soda-ash contains sulphuret of sodium, the carbonate of ammonia should first be mixed with sufficient solution of ammonia to convert the bicarbonate, always present in the common carbonate, into the neutral carbonate: the latter is without action on the alkaline sulphuret, but the bicarbonate of ammonia and sulphuret of sodium suffer mutual decomposition when placed in contact, water being also present.

After lengthened exposure to the air, soda-ash sometimes contains a little bicarbonate or sesquicarbonate of soda, which would interfere with the results of this method of alkalimetry, if present in an appreciable quantity. To detect the presence of the bicarbonate, the soda-ash is dissolved in water, mixed with an excess of solution of chloride of calcium, and the solution is filtered from the precipitate of carbonate of lime: the filtered liquid is then tested with pure solution of ammonia: if a precipitate or turbidity appears, the bicarbonate is present. The weighed sample of soda-ash must then be heated to dull redness to reduce the bicarbonate to neutral carbonate, before it can be tested by this process.

Analysis of a mixture of carbonate of soda and caustic soda.

—1; To determine the relative proportions of caustic and carbonated alkali, the carbonic acid in the mixture may be ascertained both before and after treatment with carbonate of ammonia; the amounts of caustic and carbonated alkali can be calculated from the difference in the results of the two experiments. 2. The same object may also be attained by

testing the material by both of the alkalimetric processes here described: by the first, to determine the entire proportion of alkali; and by the second, to determine the proportion of carbonic acid. 3. The most convenient way, however, is first to obtain the entire proportion of alkali by the test acid in the usual manner; and afterwards to obtain the amount of caustic alkali, by mixing an excess of chloride of barium with the material, then adding hot water, filtering the liquid, washing the carbonate of barytes on the filter, and determining the number of measures of test acid necessary for the neutralization of the filtered liquid. That number represents the amount of caustic alkali present in grains.

SECTION III.

AMMONIA.

If the ammonia whose amount is to be estimated exists in aqueous solution, and in the free state unaccompanied by ammoniacal salts except the muriate, a slight excess of hydrochloric acid is added, and the solution is evaporated to dryness in a weighed platinum capsule, by means of a water-bath. When dry, the residue is weighed, again heated in the water-bath and weighed. This is repeated so long as it suffers any loss. From the weight of the muriate of ammonia obtained, that of the ammonia is calculated: 1 part of muriate of ammonia represents 0.32077 of absolute ammonia. After the last weighing, the capsule is heated strongly, to sublime the muriate of ammonia. The loss now experienced, which should be pure muriate of ammonia, affords another datum in the calculation.

This method of estimating ammonia is not strictly exact, inasmuch as a minute quantity of muriate of ammonia volatilizes during the evaporation to dryness; but the quantity lost is so very small as not to be appreciated without an extremely delicate balance. The following, however, is a more precise method. To the ammoniacal liquid, slightly

supersaturated with hydrochloric acid, a solution of chloride of platinum is added, and the mixture is evaporated to dryness. The dry residue is digested in a mixture of two measures of alcohol, and one measure of ether, in which liquid the excess of chloride of platinum dissolves, and leaves the double chloride of platinum and ammonium undissolved. If the liquid has a yellow colour, sufficient chloride of platinum has been introduced, and the chloride of platinum and ammonium may be collected on a filter, washed with a little alcohol, dried and weighed. To control this weighing, the double chloride is calcined, in order to convert it into metallic platinum, which is also weighed: 1 part of chloride of platinum and ammonium corresponds to 0.07693 of ammonia; and 1 part of metallic platinum corresponds to 0.17390 of ammonia.

The estimation of ammonia in ammoniacal salts is performed in the following manner. A known weight of the salt is introduced into a small tubulated retort, having a tube funnel passing through a cork in the tubulure. The extremity of the funnel must reach nearly to the bottom of the retort, and be drawn out to a capillary just large enough to allow a liquid to flow through. The substance being introduced, the retort is closely connected with a receiver containing dilute hydrochloric acid, the beak of the retort just touching, but not dipping under, the surface of the liquid. A strong solution of potash is then introduced into the retort through the funnel, and heat is applied to distil the ammonia, which becomes free by the action of potash, into the receiver. If necessary, more solution of potash may be added, and afterwards water, to drive all the ammonia into the dilute acid. The solution of muriate of ammonia thus obtained in the receiver is either evaporated, and the muriate of ammonia estimated in the manner first described, or the liquid is mixed with chloride of platinum, and the ammonia estimated according to the second of the above processes.

SECTION IV.

The best mode of estimating lithia, every base except potash and soda having been previously separated from the solution, is by means of the double phosphate of soda and lithia. Pure phosphate of soda and a little carbonate of soda are added to the solution, and the whole is evaporated to dryness. On dissolving the dry mass in water, a white salt remains, insoluble in a solution of phosphate of soda, but slightly soluble in hot water. This is the double phosphate of soda and lithia. The quantity precipitated generally increases a little on standing. It is collected on a filter and washed with cold water. In consequence of the slight solubility of the double phosphate, the washing should not be prolonged beyond what is absolutely necessary. It should be heated to redness before being weighed. One part of the double phosphate contains 0.1238 of lithia.

If lithia is in combination with a volatile acid, and no other alkali is present, it may be estimated as *sulphate*, by simply adding sulphuric acid, evaporating to dryness, and heating to redness before weighing: 54.44 parts of sulphate of lithia contain 14.44 parts of lithia.

Separation of lithia from potash and soda.—When the three fixed alkalies exist together in solution, first determine the entire weight of the mixed salts by evaporation to dryness; after weighing, redissolve the residue, and estimate the potash as chloride of platinum and potassium. Through the solution filtered from the double chloride, transmit a stream of sulphuretted hydrogen gas, to remove the platinum it contains from the excess of chloride employed, evaporate, and proceed to estimate lithia as the phosphate of lithia and soda. The sum of the weights of the potash and lithia salts (ascertained by calculation) deducted from the weight of the mixed salts first determined, leaves the weight of the soda salt.

CHAPTER II.

ALKALINE EARTHS AND EARTHS PROPER, AND THEIR
METALLIC BASES.

SECTION I.

BARIUM.

BARYTES is weighed in the form of sulphate. On adding sulphuric acid to the solution containing barytes, the sulphate is immediately precipitated, but occasionally does not subside readily, and then passes through the pores of the filter. On heating the liquor, or on the addition of a little nitric or hydrochloric acid, the precipitate aggregates, and may then be collected on a filter. The sulphate of barytes is washed, dried, and ignited in a platinum or porcelain crucible. From its weight that of barium or of barytes is calculated. (See the Tables in the Appendix.)

Barytes and alkalies are separated from each other by sulphuric acid; the liquid filtered from the precipitate of sulphate of barytes is evaporated to dryness, and the alkaline sulphates may be determined by one of the processes before described.

SECTION II.

STRONTIUM.

Strontian is precipitated from its solutions for the purpose of being weighed either as sulphate or as carbonate; but both of these salts possess a slight degree of solubility in water, and hence cannot be washed by water with impunity. If the strontian is united to an acid, which when free is

soluble in alcohol, and nothing can be formed on the addition of sulphuric acid which is insoluble in weak alcohol besides sulphate of strontian, it is preferable to estimate the strontian as sulphate. The solution to be precipitated should be concentrated, mixed with alcohol and sulphuric acid, and the precipitate washed with weak alcohol, dried, ignited, and weighed.

To estimate strontian as carbonate, add to the solution an excess of carbonate of ammonia mixed with a little free ammonia, apply heat to the mixture, filter the precipitate, wash, dry, and heat it to redness. Carbonate of strontian does not part with carbonic acid at a red heat.

Strontian and barytes are separated from each other, when in solution, by hydrofluosilicic acid, which precipitates barytes (although incompletely), but not strontian. A more common, but less perfect method is, to convert the earths into dry chlorides of the metals, and then treat with alcohol, which dissolves chloride of strontium, but leaves chloride of barium undissolved.

Strontian is separated from the *alkalies* either as sulphate, by sulphuric acid, or as carbonate, by carbonate of ammonia.

SECTION III.

CALCIUM.

Lime is best precipitated from its solutions as oxalate, by means of oxalate of ammonia or oxalate of potash. The precipitate, after being washed and dried, is ignited at a red heat, when it becomes converted into carbonate of lime, which is weighed. In performing this process several precautions are necessary: 1. That the solution to be precipitated is either neutral or slightly ammoniacal, as oxalate of lime is soluble in acids. If the solution is acid, a slight excess of ammonia must be added; but this alkali may occasion the precipitation of a salt of lime, soluble in acids, but insoluble in water, and therefore precipitated on neutralization by an

alkali; such for instance, as the phosphate or arseniate. For such salts of lime the process by oxalate of ammonia cannot well be employed. Oxalate of lime, however, is nearly insoluble in acetic acid. 2. As the oxalate of lime subsides very slowly, the mixture must be boiled for some time, and allowed to stand until all the oxalate has subsided, otherwise it is impossible to filter the solution perfectly. 3. In the conversion of oxalate into carbonate of lime by ignition, if a strong heat is employed, a portion of the carbonic acid of the carbonate may be expelled, thus subjecting the estimation of the lime to a considerable deficiency: to avoid this, after weighing the ignited carbonate, add to it a few drops of a strong solution of carbonate of ammonia, again ignite at a dull-red heat, and weigh. Repeat this as long as any increase in weight is apparent.

In those salts which are soluble only in acids, and therefore precipitated from their solutions on the addition of ammonia, the lime is determined as sulphate, in a manner precisely similar to that described under the subject of strontian. If the compound of lime is soluble in *acetic acid*, then that acid is used as the solvent, and the lime is precipitated by the addition of oxalate of ammonia; as oxalate of lime is insoluble, or very nearly so, in acetic acid. The precipitated oxalate of lime is washed, dried, and ignited.

Analysis of a mixture of caustic lime and carbonate of lime.
 — To determine the amount of carbonate of lime in such a mixture, the proportion of carbonic acid is estimated by the process described under the “Analysis of Carbonates.” 22 parts of carbonic acid indicate 50·7 parts of carbonate of lime. The proportion of caustic lime is ascertained by mixing the material with a solution of muriate of ammonia, which is without action on carbonate of lime, but is decomposed by caustic lime, with formation of chloride of calcium and free ammonia. The mixture is thrown upon a filter, the carbonate of lime on the filter washed, and the lime in the filtered liquid precipitated as oxalate. Or, if extreme accuracy is not required, the free ammonia in the filtered liquid is neutralized by the test acid employed in alkalimetry (page

306.); each measure of the alkalimeter requisite for the neutralization indicates the presence of 0.92 grain of caustic lime.

Separation of lime from strontian. — When these two earths exist together in solution, their separation may be effected in the following manner. They are first converted into carbonates by the addition of carbonate of soda or potash; the precipitated carbonates are filtered, washed, and dissolved in dilute nitric acid to be converted into nitrates. The solution of the nitrates thus obtained is evaporated to dryness, to expel the last traces of nitric acid, and the residue is treated with alcohol, which dissolves nitrate of lime, but leaves nitrate of strontian undissolved. The nitrate of strontian is collected on a filter, and washed with alcohol. When washed, the salt may be dissolved in water, and the strontian estimated as sulphate: the lime of the nitrate in the filtered alcoholic liquid is estimated as oxalate.

Separation of lime from barytes. — On adding sulphuric acid to the solution containing these two earths, both sulphate of barytes and sulphate of lime are precipitated; but from the slight solubility of sulphate of lime in water, it may be completely separated from sulphate of barytes by a long-continued washing on a filter. A solution of oxalate of ammonia is added to the filtered liquid, which should be concentrated by evaporation before the precipitated oxalate of lime is collected on a filter.

Lime is separated from the *fixed alkalis* by oxalate of ammonia; on evaporating the liquid filtered from the precipitated oxalate of lime to dryness, and calcining the dry salt, the excess of oxalate of ammonia is expelled, together with any other ammoniacal salt which may be present, leaving a residue, which may be treated in the usual way to obtain the alkali.

The method of analyzing limestones will be described under the “Analysis of Carbonates.” (pp. 435)

SECTION IV.

MAGNESIUM.

A solution of phosphate of soda, to which pure ammonia or its carbonate has been previously added, is employed to precipitate magnesia from its solutions, for the purpose of being weighed. The magnesia then falls in the state of phosphate of magnesia and ammonia ($2 \text{ Mg O}, \text{NH}_4 \text{ O}, \text{PO}_5 + 12 \text{ HO}$). Several precautions are necessary in this operation. The solution should be concentrated to a small bulk by evaporation; it should be quite cold, and either neutral or slightly ammoniacal, as the precipitated phosphate of magnesia and ammonia is soluble in free acids. Even carbonic acid, and, according to Stromeyer, alkaline carbonates, dissolve it to a small extent. If free carbonic acid exists in the solution, it must therefore be expelled by boiling; and if alkaline carbonates are present, they should be decomposed by the addition of hydrochloric acid: the solution is afterwards boiled, and the excess of acid neutralized by pure ammonia. Phosphate of magnesia and ammonia is also slightly soluble in pure water: hence, if the proportion of magnesia in the solution is small, no precipitate is at first produced on the addition of phosphate of soda with ammonia. The precipitate appears, however, on stirring for some time, which should never be omitted before filtration. Although soluble in pure water, phosphate of magnesia and ammonia is not soluble in water which contains phosphate or muriate of ammonia in solution. A dilute solution of the latter salt is hence advantageously employed to wash the phosphate when collected on a filter. When dried and ignited, the muriate of ammonia is expelled, and the phosphate of magnesia and ammonia becomes reduced to phosphate of magnesia, $2 \text{ Mg O} + \text{PO}_5$, containing 36.67 per cent. of magnesia, in which state this earth is weighed.

Magnesia may also be precipitated in the form of carbonate, by the fixed alkaline carbonates; but owing to the tendency

of the latter to form soluble double salts with the carbonate of magnesia, this method of estimating magnesia is not more certain than the preceding. A solution of carbonate of soda (this salt being preferable to carbonate of potash) is added to the hot magnesian solution, and the liquid boiled until the precipitate is no longer bulky and light, but has become granular and heavy. As the presence of ammoniacal salts interferes with the precipitation of magnesia in the state of carbonate, these should be expelled from the solution by boiling with a sufficient quantity of carbonate of soda, until the odour of ammonia is no longer perceptible. The precipitate, if granular, and comparatively dense, is then collected on a filter, and the filtered liquid is evaporated to dryness. On treating the residue of the evaporation with boiling water, a minute quantity of carbonate of magnesia generally remains undissolved, which should be added to that already on the filter. The precipitate, when washed, is dried, ignited strongly to expel carbonic acid, and weighed as pure magnesia.

If magnesia exists in solution unmixed with other fixed bases, and not combined with a fixed acid, it may be estimated in the state of sulphate. The solution is evaporated to dryness, and if any ammoniacal salts are present, heated to redness in a platinum crucible. The residue is treated with dilute sulphuric acid, again heated to redness, and weighed when cold. If the magnesia already exists as sulphate, the addition of sulphuric acid is of course unnecessary.

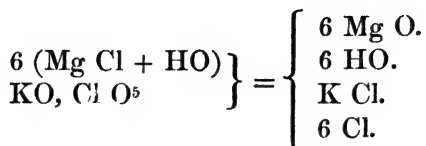
The *separation of magnesia from lime* can be effected by oxalic acid. Ammonia in very slight excess is added to the solution of the two earths in hydrochloric acid, a previous addition having been made of muriate of ammonia, to prevent the precipitation of magnesia by ammonia. If the solution is very acid, a sufficient quantity of ammoniacal salt will be formed for the purpose, and the addition of muriate of ammonia is then unnecessary. If ammonia causes a precipitate of magnesia, this must be redissolved in hydrochloric acid, and a slight excess of the alkali again added, on which no precipitation will occur. The lime is then precipitated by

oxalic acid, or by oxalate of ammonia, the oxalate of lime is collected on a filter, and magnesia is precipitated from the filtered solution as carbonate or ammonio-phosphate of magnesia. After the precipitation of lime as oxalate, the solution may deposit oxalate of magnesia on evaporation, if a large excess of oxalate of ammonia has been added: this is prevented by adding hydrochloric acid in very slight excess before the evaporation. If the magnesia in solution is to be precipitated as phosphate, the hydrochloric acid must be neutralized by ammonia before precipitation.

Döbereiner has proposed an excellent process for the separation of magnesia and lime, by the use of chlorate of potash. The solution of the two earths in hydrochloric acid is evaporated to dryness, and the residue is calcined in a platinum crucible, to expel the excess of hydrochloric acid. Powdered chlorate of potash is then added so long as the evolution of chlorine is perceptible. On treating the dry mass with water, chloride of calcium and chloride of potassium are dissolved, and a residue of pure magnesia remains, which is filtered, washed, ignited, and weighed. The lime in the filtered solution may be precipitated by oxalate of ammonia.

When heated to redness alone, hydrated chloride of magnesium decomposes into magnesia and hydrochloric acid. Hydrated chloride of calcium, however, resists decomposition in this manner, or, at least, at the temperature necessary for the decomposition of chloride of magnesium. Hence, when a mixture of the two hydrated chlorides is ignited, on treating the calcined mass with water, chloride of calcium alone redissolves, if the ignition has been continued a sufficient length of time for the chloride of magnesium to be fully decomposed. Magnesia then remains as an insoluble residue. It is, however, with difficulty that this decomposition of the hydrated chloride of magnesium can be completely effected alone; but by the addition of chlorate of potash, as in Döbereiner's process for the separation of lime from magnesia, it is remarkably facilitated. This arises from the decomposition of the hydrochloric acid, as it is evolved from the hydrated chloride, by the oxygen of the chlorate of potash; water and

chlorine being the products of the decomposition. Six equivalents of hydrated chloride of magnesium, and one of chlorate of potash, produce six equivalents of magnesia, six of water, one of chloride of potassium, and six of chlorine: or expressed in symbols: —



Separation of magnesia from the fixed alkalis.—One of the best means of effecting the separation of magnesia from the fixed alkalis is the following: — The magnesia is first precipitated by subphosphate of ammonia, and the precipitated phosphate is filtered, washed, ignited, and weighed: acetate of lead is added to the filtered solution, to separate phosphoric acid (from the excess of phosphate of ammonia employed), and the precipitated phosphate of lead is separated by filtration. The lead in excess now existing in the solution is precipitated by supersaturation with sulphuretted hydrogen gas; the solution is filtered and evaporated to dryness. The residue of the evaporation consists of acetates of the alkalis, which may be converted into sulphates or chlorides by the addition of sulphuric or hydrochloric acid, and estimated by methods already described.

Liebig recommends a process for the separation of magnesia from the fixed alkalis, founded on the higher basic properties of barytes than magnesia. The solution containing magnesia and alkalis is mixed with muriate of ammonia, evaporated to dryness, calcined, and the residue is dissolved in a small quantity of water. To this solution, saturated barytes-water is added, and the magnesia thereby precipitated is collected on a filter: barytes is separated from the filtered liquid by sulphuric acid; the solution is filtered, evaporated to dryness, and the residue calcined with a little carbonate of ammonia. (page 301.) Neutral alkaline sulphates remain, which may then be weighed.

Berzelius has recommended the following process for the separation of magnesia from the fixed alkalis, when existing in the state of chlorides, as is generally the case in mineral waters. The concentrated solution of the chlorides is mixed with protoxide of mercury (red oxide), and then evaporated to dryness. The chloride of magnesium and oxide of mercury undergo mutual decomposition, becoming magnesia and chloride of mercury; the latter combines with the alkaline chloride to form a double salt. The dry mass is treated with water, the solution is filtered, evaporated to dryness, and the residuc calcined to expel all the chloride of mercury. What remains after the chloride of mercury is expelled, is the alkaline chloride, which may be weighed. The portion insoluble in water, consisting of a mixture of magnesia with the excess of oxide of mercury, is ignited strongly, in order to expel the latter. Pure magnesia then remains, in a fit state to be weighed.

SECTION V.

ALUMINUM.

For the purpose of being weighed, alumina is precipitated from its solutions by ammonia or carbonate of ammonia. As pure ammonia exercises a slight solvent action on alumina, the carbonate should be used in all cases where it is admissible. When pure ammonia must be employed, however, the alumina is completely precipitated on boiling the solution for a short time. The precipitate is very bulky, and must be washed with hot water.

If alumina is to be precipitated from its solution in the caustic fixed alkalis, the alkali may be first saturated with hydrochloric acid, of which a sufficient quantity is added to redissolve the alumina at first precipitated, and a solution of carbonate of ammonia, or ammonia, is then added to precipitate alumina: or the alkaline solution of alumina may be simply mixed with an excess of muriate of ammonia, which gives

rise to the production of chloride of potassium or sodium and free ammonia, with precipitation of alumina. The mixture should be heated, in order that the alumina may be completely precipitated.

Separation of alumina from magnesia, lime, and the fixed alkalies. — Supposing these bases to exist together in solution, their separation can be effected in the following manner. Muriate of ammonia is first added to the solution, to prevent the precipitation of magnesia by ammonia, which alkali is next added to precipitate *alumina*. If the solution was previously very acid, the addition of muriate of ammonia is unnecessary, as a sufficient quantity of an ammoniacal salt will be formed for the purpose, by the neutralization with ammonia. The ammonia should be perfectly free from carbonate, otherwise carbonate of lime will be formed. The precipitate of alumina should be filtered as rapidly as possible, to prevent absorption of carbonic acid from the atmosphere by ammonia, and washed with distilled water. To the liquid filtered from the precipitate of alumina, oxalate of ammonia is added to precipitate oxalate of *lime*, which is collected on a filter, washed, and converted into carbonate by ignition in a platinum crucible. (page 315.) The precipitate of alumina produced by ammonia, carries down a little magnesia with it, whatever amount of muriate of ammonia may exist in the liquid: this magnesia is separated by dissolving the alumina in caustic potash; the magnesia remains undissolved by the alkali. To perform this, the precipitate of alumina, after being washed, should be dissolved in hydrochloric acid; an excess of caustic potash is then added to the solution, and the mixture heated in a porcelain or platinum capsule. The alumina, at first precipitated by the potash, redissolves in the excess of alkali, leaving magnesia undissolved, which is collected on a filter and washed. To the alkaline solution of alumina, hydrochloric acid is added until the precipitate of alumina at first produced is entirely redissolved; a solution of carbonate of ammonia in excess is then added to throw down the alumina. The small quantity of magnesia on the filter should be dissolved in hydrochloric acid, and this solu-

tion added to that filtered from the oxalate of lime, which contains the greater part of the magnesia, together with the alkalis. Processes for the separation of magnesia from alkalis have already been described.

When it is required to separate alumina from magnesia only, this may be accomplished by the same means as in the process just described, where lime and alkalis also are supposed to be present. Muriate of ammonia is first added to the solution, and then caustic ammonia. The small quantity of magnesia precipitated with the alumina is separated by hydrochloric acid and potash, in the manner described. The magnesia undissolved by potash is dissolved in hydrochloric acid, and added to the solution filtered from the precipitate by ammonia. From this solution magnesia may be precipitated, as the ammonio-phosphate. (page 318.)

To separate alumina from lime only, the former is precipitated from the solution containing these earths by ammonia, which must be quite free from carbonate of ammonia, otherwise carbonate of lime will also be precipitated. The alumina should be collected on a filter as rapidly as possible, to prevent absorption of carbonic acid from the atmosphere by ammonia. After the filtered ammoniacal solution has been boiled to expel most of the excess of ammonia, the lime it contains may be precipitated by oxalate of ammonia or oxalic acid.

From *barytes*, alumina is separated by precipitating the former earth as sulphate, by sulphuric acid or a soluble sulphate.

To separate alumina and *strontian*, the former may be precipitated by ammonia, the access of air being avoided as much as possible, to prevent the formation of carbonate of strontian.

Alumina and the *fixed alkalis* may be separated by adding carbonate of ammonia, or free ammonia, to the neutral or acid solution. On evaporating the solution filtered from the precipitate of alumina to dryness, and calcining the residue, the ammoniacal salts which are present volatilize, leaving the salts of the fixed alkalis.

Solution of aluminous minerals.—The solution of a few minerals, which consist entirely or chiefly of alumina, is very difficult to effect by ordinary means. M. Rose has shown that when corundum and aluminates * are reduced to a fine powder, they may be completely dissolved by first fusing them with an excess of bisulphate of potash, and then digesting the fused mass in water. The mineral should be pounded in a steel crushing-mortar, and not in an agate mortar, that no silica may be acquired by abrasion of the latter: it should be reduced to a further state of division by sifting through very fine muslin. A platinum crucible may be employed for the fusion with bisulphate of potash. From the solution of the fused salt in water, alumina may be precipitated by ammonia; but as a subsulphate of alumina is precipitated, instead of pure alumina, the precipitate should be separated by filtration, dissolved in hydrochloric acid, and again precipitated by ammonia. It is then pure alumina, which may be washed, ignited, and weighed.

SECTION VI.

Potash and ammonia are both employed to precipitate yttria from its solutions, in the quantitative determination of that earth. Hydrate of yttria falls, which may be collected on a filter, washed, ignited, and weighed as pure yttria. Except when yttria is in the state of chloride, potash is a better precipitant to employ than ammonia, as the latter alkali precipitates subsalts of yttria from the sulphate and nitrate.

The insolubility of yttria in potash affords the means of separating it from *alumina*, and its being precipitated by ammonia, although in the presence of an ammoniacal salt, from *magnesia*, *lime*, *barytes*, *strontian* and the *alkalies*.

* The minerals in which alumina acts the part of an acid are called *aluminates*.

SECTION VII.

THORINUM.

Thorina is separated from most other bodies by precipitation as double sulphate of thorina and potash. A boiling saturated solution of sulphate of potash is added to the solution containing thorina, the mixture is allowed to cool, and the precipitate is filtered and washed with a cold saturated solution of sulphate of potash, in which the double salt is quite insoluble. After washing with solution of sulphate of potash, boiling water is poured on the filter, to dissolve the salt, the thorina of which is then precipitated by pure potash.

Thorina is separated from *alumina* by its insolubility in potash; and from *magnesia* and *lime* by being precipitated by ammonia in the presence of an ammoniacal salt. It is separated from alkalies by ammonia, which completely precipitates thorina.

SECTION VIII.

GLUCINUM.

Ammonia is the reagent employed to precipitate glucina from its solutions when unaccompanied by other matters which are precipitated by ammonia. A voluminous precipitate of glucina falls, which contracts considerably on drying.

Glucina is separated from *thorina* and *yttria* by its solubility in potash, and from *alumina* by its solubility in carbonate of ammonia. To separate glucina from alumina, add a large excess of a saturated solution of carbonate of ammonia to the mixed solutions of the two earths, and allow the whole to stand for some time, with occasional agitation. When the precipitate of alumina no longer appears to decrease in bulk,

collect it on a filter, wash, ignite, and weigh it, and evaporate the filtered solution to dryness. As the carbonate of ammonia volatilizes, the glucina is deposited: when the dry mass is heated to redness, to expel ammoniacal salts, it leaves pure glucina, the weight of which may then be ascertained.

A process has been recommended for the separation of alumina and glucina, which is said to be preferable to the preceding. Both glucina and alumina are soluble in a concentrated solution of potash; but if the alkaline solution is diluted considerably with water, and boiled, all the glucina is precipitated, while the alumina still remains in solution. The process is the following. Both earths are dissolved, with the assistance of heat, in a concentrated solution of potash; the solution is cooled and diluted with water. The precipitate which falls (glucina) is filtered and washed, and the filtered solution is boiled to precipitate the remaining glucina. The alumina which remains dissolved may be estimated in the usual manner. (page 322.)

Berzelius* supposes it probable that glucina precipitated by ebullition from a dilute solution of potash, contains potash in chemical combination, for it is insoluble in cold alkaline ley after this operation; but by washing, all the potash it may contain is removed, and it again becomes soluble in the cold ley.

Glucina may be separated from *magnesia* by a process similar to that described for the separation of alumina from *magnesia*. The only difference is, that while caustic ammonia or carbonate of ammonia may be used indiscriminately to precipitate alumina, caustic ammonia only should be employed for glucina.

Glucina is separated from *lime*, *strontian*, *barytes*, and the *fixed alkalies*, by methods the same as those by which alumina is separated from the same bodies.

* *Rapport Annuel*, 1841, 2^e Année, p. 79. (Paris edition.)

SECTION IX.

ZIRCONIUM.

Zirconia is best precipitated from its solutions by potash. Ammonia may also be employed; but this alkali sometimes precipitates subsalts instead of pure zirconia. The precipitate is washed, dried, ignited with care, and weighed. Zirconia may be precipitated by sulphate of potash in the same manner as thorina. For that purpose, it is best to add sulphate of potash *in crystals* to the solution containing zirconia. The precipitate which falls is a double sulphate of zirconia and potash. If all excess of acid present in the solution is neutralized with potash, zirconia may be completely precipitated by sulphate of potash. As the precipitate is partly soluble in pure water, it should be washed with water rendered alkaline by the addition of a little caustic ammonia. On boiling the double sulphate of zirconia and potash with a solution of pure potash, hydrate of zirconia remains, which may be washed, ignited, and weighed.

CHAPTER III.

METALS PROPER, NOT PRECIPITATED BY SULPHURETTED
HYDROGEN FROM THEIR ACID SOLUTIONS.

SECTION I.

POTASH or soda is the best precipitant for the oxides of cerium, ammonia having a tendency to throw down subsalts instead of the pure oxides. If the solution previously contained *protoxide* of cerium, the precipitate of protoxide produced by potash becomes converted by calcination into the *peroxide*, from the weight of which the amount of protoxide originally present must be calculated.

The oxides of cerium are separated (though not completely) from *glucina* and *alumina* by the insolubility of the former in caustic potash; and from *magnesia* and *lime* by ammonia.

Valerianic acid has been recommended as a means of separating peroxide of cerium from the peroxide of the metal *didymium*, recently discovered by M. Mosander. When valerianic acid is added to a neutral and concentrated solution of the peroxides of cerium and didymium, valerianate of the peroxide of cerium is precipitated, while the didymium remains in solution. The precipitated valerianate is slightly washed, dried, and calcined: by calcination with access of air, it is converted into the peroxide of cerium. (M. Buonaparte.)

SECTION II.

MANGANESE.

Carbonate of potash is the reagent usually employed to precipitate protoxide of manganese from its solutions. The

solution should be boiling at the time of the precipitation. Carbonate of protoxide of manganese falls, which may be collected on a filter. When the solution filtered from the precipitated carbonate is evaporated until the residue is dry, a little more carbonate generally remains undissolved when the dry residue is treated with hot water; this portion is to be added to that already on the filter.

As carbonate of manganese is slightly soluble in ammoniacal salts, the whole oxide of manganese is not precipitated, if these are present in the solution, until a sufficient quantity of carbonate of potash has been added to decompose all ammoniacal salts. To effect their complete decomposition, the liquid should be mixed with carbonate of potash and evaporated nearly to dryness, fresh additions of the alkaline carbonate being made so long as any odour of ammonia is perceived. By this means ammoniacal salts may be completely expelled from the solution.

After washing and drying, the carbonate of manganese is heated to redness in an open platinum crucible: it then parts with carbonic acid, and requires oxygen from the air, being converted into the red oxide of manganese (manganoso-manganic oxide, $\text{Mn O} + \text{Mn}_2 \text{O}_3$), from the weight of which that of protoxide or deutoxide, originally present in the substance under examination, may be calculated.

As the red oxide of manganese absorbs a little more oxygen while being cooled, M. Ebelmen recommends the reduction of the red oxide by means of hydrogen gas, with the assistance of a red heat, to the state of protoxide, in which form the manganese is weighed. For this and several other operations, he uses, in the place of the glass bulbed tube (*c d c*, fig. 20., page 345.), a small platinum crucible; through the lid of which passes a platinum tube large enough to admit a small glass tube, by which the hydrogen gas is conveyed to the crucible.

Separation of protoxide of manganese from alumina.—

1. Protoxide of manganese may be separated from alumina by boiling the solution which contains these substances with an excess of caustic potash: of the mixture of oxide of manganese and alumina at first precipitated, the latter alone dis-

solves in the excess of alkali. The alumina in solution may then be estimated in the usual manner (page 322.); and the oxide of manganese, insoluble in caustic potash, may be dissolved in hydrochloric acid, and precipitated as carbonate, by carbonate of potash.

2. Protoxide of manganese and alumina may also be separated by ammonia, muriate of ammonia having been first added to the solution, to prevent the precipitation of protoxide of manganese.

Separation of protoxide of manganese from magnesia and lime.—When the amount of manganese present is relatively small, the following process is recommended. A sufficient quantity of muriate of ammonia is first added to the solution (unless it contains a large excess of acid) to prevent precipitation by ammonia, which is next added, and then an excess of hydrosulphate of ammonia to precipitate sulphuret of manganese. The precipitated sulphuret is collected on a filter, washed with water containing a little hydrosulphate of ammonia, and dissolved in pure hydrochloric acid: sulphuretted hydrogen is thus developed, to expel which, the solution is heated until it becomes inodorous. The solution is now filtered, and the manganese precipitated by carbonate of potash. The solution filtered from the sulphuret of manganese, containing lime and magnesia, is slightly acidified by hydrochloric acid, boiled to expel sulphuretted hydrogen, and filtered. The filtered solution is then supersaturated with ammonia: lime is precipitated as oxalate, by oxalate of ammonia or oxalic acid, and afterwards magnesia, as the ammonio-phosphate.

When protoxide of manganese constitutes the chief ingredient, the following process is preferable. Carbonates of manganese and of the two earths are precipitated by a fixed alkaline carbonate, the solution being boiling at the time of precipitation. The precipitate is ignited at a dull red heat, to convert the carbonate of manganese into the manganoso-manganic oxide, and is then treated with very dilute nitric acid. This acid slowly dissolves the lime and magnesia with effervescence, leaving the oxide of manganese

unacted on, which may be collected on a filter, washed, again ignited, and weighed. Any trace likewise of manganese dissolved by the nitric acid can be precipitated by hydrosulphate of ammonia, after neutralizing the acid by caustic ammonia. The lime and magnesia may be separated from each other by a process already described.

VALUATION OF PEROXIDE OF MANGANESE.

A simple and expeditious process for the determination of the commercial value of the higher oxides of manganese, is of some importance, from the extensive applications of these oxides in the arts. Of several processes which have been devised for this purpose, the following is, I believe, the most convenient. It is founded on the circumstance, that the value of these oxides is exactly proportional to the quantity of free chlorine which they produce when dissolved in hydrochloric acid, and the chlorine can be estimated by the quantity of protosulphate of iron which it oxidizes.

Twenty-five grains of the powdered oxide of manganese to be examined are weighed out, and also 158.5 grains of crystallized sulphate of iron (copperas).^{*} The oxide of manganese is placed in a bason with half an ounce of water and a very small quantity of hydrochloric acid; a little copperas is then introduced, and a gentle heat applied to the bason. More hydrochloric acid and copperas are added from time to time, the former to dissolve the oxide of manganese, and the latter to absorb the chlorine as it is evolved. Immediately a drop of the liquid ceases to afford a blue precipitate with the red prussiate of potash[†], a little more copperas is introduced; and this is continued till the liquid, after ebul-

^{*} Clean crystals of the salt, bruised in a mortar, and dried by strong pressure between folds of cloth; or, what is better, the small crystals deposited from a tolerably strong solution of copperas, which has been filtered and allowed to stand without having free access to the air; the supernatant liquid having been drained off, the crystals may be dried in the air upon blotting-paper.

[†] The red prussiate of potash gives a blue precipitate (prussian blue) with the protoxide of iron only, and not with the peroxide; hence the production of a blue precipitate is an indication that a sufficient quantity of copperas has been applied. In applying the red prussiate as a test, it is convenient to have a white plate spotted over with small drops of its solution, very dilute, which are touched with a drop of the liquid to be tested, taken out on the point of a glass rod.

lition for five minutes, and addition of an ounce measure or more of hydrochloric acid, gives a faint but permanent blue precipitate with the red prussiate of potash. The sulphate of iron is then present in slight excess. By weighing what remains of the sulphate of iron, the quantity added is ascertained; say m grains. If the whole manganese were peroxide, it would require 158.5 grains of sulphate of iron, and that quantity would, therefore, indicate 100 per cent. of peroxide in the specimen: but if a portion of the manganese only is peroxide, it will consume a proportionally smaller quantity of the sulphate, which quantity will give the proportion of the peroxide, by the proportion, as $158.5 : 100 :: m : \text{per-centage required}$. The per-centage of peroxide of manganese is thus obtained by multiplying the number of grains of sulphate of iron peroxidized by 0.6309.

The following modification of the preceding process is somewhat easier and quicker of execution than the above, and may give results of more certainty, not being subject to the slightest loss of chlorine, which often occurs with inexperienced hands in the other process.

1. Twenty-five grains of the sample of oxide of manganese, finely powdered, are introduced into a small flask, and mixed at once with the quantity of crystallized protosulphate of iron which is equivalent to 25 grains of pure peroxide of manganese, that is, with 158.5 grains; an ounce measure of strong muriatic acid is then added, and the mixture is quickly raised to the boiling point. The flask should be closed with a cork having a small slit in the side to allow the escape of vapour. If the sample is pure peroxide, the whole of the 158.5 grains of protosulphate of iron will be peroxidized; but if not, the quantity of the protosulphate which remains unaltered is proportional to the amount of impurity present in the sample.
2. To ascertain the quantity of protosulphate in excess, the hot acid solution, when all the manganese is dissolved, is mixed with a solution in water of known strength of bichromate of potash (purified by two or three successive crystallizations), added by small portions at a time until the mixture no longer gives a blue precipitate with a solution of red

prussiate of potash, but a dark green colour, which is an indication that the bichromate has peroxidized the remaining protosulphate of iron; and the quantity of the bichromate necessary for this purpose is proportional the excess of protosulphate which is required.

The solution of bichromate of potash employed in this experiment may be made very weak, and be poured from a common alkalimeter, graduated into 100 equal parts (as figured at p. 306.); or else a much stronger solution may be made use of, and the quantity applied be noted by weight, instead of by measure. For use with the common alkalimeter, the solution of the bichromate (if pure) may contain 28.94 grains in 100 measures of the alkalimeter. That quantity peroxidizes 158.5 grains of crystallized protosulphate of iron; therefore each measure of the alkalimeter required for the peroxidation of the excess of protosulphate indicates one per cent. of impurity in the sample. Before adding the solution of the bichromate, it is convenient to transfer the boiling manganese solution from the flask in which it was made to a bason, the flask being washed out with a little hot water, and the washings added to the solution of manganese. The liquid should be kept at a moderate heat while being mixed with the bichromate.

This operation should be performed as rapidly as possible, to prevent the peroxidation, by the air, of any appreciable quantity of the protoxide of iron. For the same reason also, the little flask in which the manganese is dissolved in hydrochloric acid with copperas, is closed with a cork, a small slit being made through which the vapour can escape.

The substitution of chlorate of potash for the bichromate in the preceding operation has been proposed, but I believe the bichromate to be the most trustworthy: 11.73 grains of the chlorate may be dissolved in 100 alkalimeter measures; each measure of the solution required for the peroxidation of the iron then indicates one per cent. of impurity, supposing .25 grains of manganese and 158.5 of copperas to be operated on.

(See a process for the complete analysis of ores of manganese in the Appendix.)

SECTION III.

IRON.

This metal is best weighed in the state of peroxide, as obtained by precipitation from its solution by ammonia, potash, or by carbonate of potash or soda. If not already existing in solution as peroxide, but as protoxide or black oxide, it must be converted into the peroxide by being heated with a little nitric acid, until ruddy fumes of nitric oxide are no longer evolved, and the black colour sometimes acquired by the liquid on the addition of nitric acid has disappeared. The amount of metal, protoxide, or black oxide, which was formerly contained in the substance analyzed, is calculated in such a case from the quantity of peroxide obtained. Caustic ammonia is the best precipitant to employ, as the peroxide of iron precipitated by potash always carries down with it some portion of that alkali, which is not removed by washing without great difficulty; and the fixed alkaline carbonates retain a little peroxides in solution at common temperatures. A strong solution of carbonate of ammonia is capable of retaining in solution a large quantity of peroxide of iron; but if the liquid is greatly diluted, the whole of the peroxide of iron is precipitated. As much of the precipitated peroxide as possible is transferred, when washed and dried, to a crucible for ignition, the filter with the remaining peroxide being carefully burned outside the crucible (as described at page 12.), to prevent the reduction of any portions of oxide to the state of protoxide or black oxide by the carbonaceous matter of the filter.

Iron may be separated from several other bodies by precipitation as sulphuret, by hydrosulphate of ammonia. If the solution contains any free acid, it must first be neutralized by ammonia, which alkali may be added in slight excess, as the precipitation of a small quantity of peroxide of iron does not interfere with the result. A sufficient quantity of hydrosulphate of ammonia is then added, the precipitate is filtered,

washed with water containing a little hydrosulphate of ammonia, and dissolved in pure hydrochloric acid. The solution thus obtained is heated to expel sulphuretted hydrogen, a little nitric acid is added to peroxidize the iron, the solution is filtered if necessary, and the peroxide of iron is precipitated by ammonia.

Separation of peroxide of iron from protoxide of manganese.

— 1. In the process generally preferred for the accurate estimation of these oxides, when contained together in a solution, their separation is effected by means of a neutral succinate or benzoate of an alkali, which precipitates peroxide of iron as succinate or benzoate, in a neutral solution, but not protoxide of manganese. If any iron exists in solution as protoxide, it must first be converted into peroxide by gently heating the solution with a little nitric acid or aqua regia.

If the solution is acid, it must be rendered neutral by ammonia, muriate of ammonia being previously added to prevent the precipitation of protoxide of manganese. A very slight excess of ammonia may be added, so that a trace of peroxide of iron remains undissolved when the solution is gently heated. Solution of crystallized succinate of soda, of neutral succinate of ammonia, or of benzoate of ammonia, may be used as the precipitant. A very bulky precipitate of benzoate or succinate of peroxide of iron falls, which, after being filtered and washed, is decomposed by pouring caustic ammonia on it, while still on the filter. By this, a large portion of the benzoic or succinic acid is removed, in the state of a soluble benzoate or succinate of ammonia, peroxide of iron, or rather a subsalt of that oxide, remaining on the filter, which last is dried, ignited with exposure to air, and weighed as peroxide. The object in removing the organic acid by ammonia is to avoid the reduction of the oxide during ignition. From the solution filtered from the precipitated succinate or benzoate, protoxide of manganese may be precipitated by carbonate of soda.

2. Peroxide of iron and protoxide of manganese may also be separated by boiling the solution of the two oxides

(chlorides) in hydrochloric acid with carbonate of barytes or carbonate of lime. The perchloride of iron in solution is decomposed by the earthy carbonate, with precipitation of peroxide of iron, and the formation of a corresponding quantity of chloride of barium or chloride of calcium; while protochloride of manganese, on the contrary, is not affected by the earthy carbonate. The latter is added to the solution of the two oxides in hydrochloric acid so long as effervescence of carbonic acid occurs. When a sufficient quantity has been added, the mixture is boiled for a short time, and filtered. The precipitate of peroxide of iron with the excess of earthy carbonate is then dissolved in hydrochloric acid, and if carbonate of lime has been used, ammonia is added to reprecipitate peroxide of iron, avoiding exposure to the air as much as possible, to prevent the absorption of carbonic acid and formation of carbonate of lime. If carbonate of barytes has been used instead of carbonate of lime, barytes may first be separated from the solution in hydrochloric acid by sulphuric acid, and peroxide of iron afterwards from the solution filtered from the sulphate of barytes by ammonia.

The solution filtered from the precipitate of peroxide of iron and the excess of earthy carbonate contains chloride of manganese, together with chloride of calcium or chloride of barium. If the former, oxide of manganese is separated from lime (oxide of calcium) by one of the processes described at page 331.; if the latter, barytes (oxide of barium) may first be separated from the solution as sulphate, by adding sulphate of soda, and after filtering the solution, the the oxide of manganese may be precipitated as carbonate by carbonate of potash.

A process similar to the above is frequently practised in the separation of peroxide of iron from other oxides whose solutions in hydrochloric acid are not decomposed when boiled with carbonate of lime or barytes. Two particular precautions are necessary to be adopted in this process: 1., that neither ~~neither~~ sulphuric, phosphoric, arsenic, nor boracic acid is present in the solution; and, 2., that all the iron exists in the

state of peroxide, as salts of the protoxide of iron are not decomposed by carbonate of lime.

Separation of protoxide of iron from peroxide of iron.—On the property possessed by salts of the protoxide of iron to resist decomposition by an earthy carbonate, is founded a process for the separation of peroxide from protoxide of iron, when existing together in solution. When boiled with carbonate of barytes, the salt of the peroxide only is decomposed; the solution filtered from the precipitated peroxide and the excess of carbonate of barytes is boiled with a little nitric acid, to convert the protoxide of iron into peroxide, which last is precipitated by ammonia, after the barytes has been separated by sulphuric acid.

(For another mode of separating protoxide of iron and peroxide of iron, see a note to the description of the mode of estimating phosphoric acid in soils.)

Separation of peroxide of iron from yttria.—Yttria and peroxide of iron may be separated by means of oxalate of potash, which produces with yttria, in a neutral solution, a precipitate consisting of the double oxalate of yttria and potash. The whole of the iron should remain in solution. The precipitate does not appear immediately, and the mixture should be allowed to stand for twenty-four hours in a warm place before being filtered. By being heated to redness, the double oxalate is converted into a mixture of yttria and carbonate of potash. As thus obtained, yttria is too finely divided to be collected on a filter after being mixed with water, on which account it is necessary to dissolve the mixture in hydrochloric acid, to dilute the solution largely with water, to precipitate by ammonia, and to wash the precipitated yttria with boiling water. It may then be ignited and weighed. (Dr. Scheerer.)

The preceding process may also be followed in the separation of peroxide of iron from protoxide of cerium and oxide of lanthanum.

Separation of peroxide of iron from alumina.—1. Peroxide of iron may be separated from alumina by adding an excess of caustic potash to the solution. The alumina contained in

the precipitate redissolves, and may be separated, after filtration, by neutralizing the alkaline solution with hydrochloric acid, and precipitating by carbonate of ammonia.

2. The following process for the separation of peroxide of iron and alumina will probably be found more advantageous than the preceding in some cases. Sulphite of ammonia is added to the solution containing these bodies, or else the mixed hydrates in a moist state are digested in an aqueous solution of sulphurous acid, and the mixture is boiled until sulphurous acid is no longer disengaged. The reddish-brown colour of the liquid disappears, the sulphurous acid reduces the peroxide of iron to protoxide of iron, and the whole of the alumina is precipitated, while all the iron remains in solution. The access of air should be avoided as much as possible. When the liquid has cooled, and the precipitate subsided, the supernatant liquid is decanted to a filter and replaced by hot water; the precipitate is then thrown on a filter and washed. If phosphoric acid is present, it is carried down by the alumina in this process, but arsenic acid is not.

Separation of peroxide of iron from magnesia.—These bodies are separated by a process similar to that described for the separation of peroxide of iron from protoxide of manganese by means of a neutral benzoate or succinate of an alkali. Instead of neutralizing any excess of acid in the solution carefully, as when manganese is present, an excess of ammonia may be added at once, having made a previous addition of muriate of ammonia, unless the quantity of free acid is considerable. The precipitate, which consists of peroxide of iron with merely a trace of magnesia, is filtered, redissolved in hydrochloric acid, and the solution thus obtained is rendered exactly neutral by ammonia. Peroxide of iron is then precipitated as succinate or benzoate, and the liquid filtered from this precipitate is added to that filtered from the precipitate by ammonia, which contains the greater part of the magnesia. From the mixed solutions magnesia may be precipitated as the ammonio-phosphate.

If extreme accuracy is not important, the solution may be mixed, first with a quantity of muriate of ammonia, and then

with caustic ammonia, to precipitate the peroxide of iron. The magnesia carried down by the peroxide of iron is a mere trace, when the solution contains a large quantity of an ammoniacal salt.

Separation of peroxide of iron from barytes.—The barytes is first precipitated as sulphate, by adding a solution of sulphate of soda; and from the filtered solution peroxide of iron is precipitated in the usual manner.

Separation of peroxide of iron from lime, strontian, and the alkalis.—This is easily effected by caustic ammonia, which precipitates peroxide of iron only. In the cases of lime and strontian, the free access of the air should be avoided, to prevent the precipitation of carbonate of lime or strontian, through the absorption of carbonic acid.

ANALYSIS OF CLAY IRONSTONE.

The ordinary constituents of this ore are,—carbonic acid, silica, protoxide and peroxide of iron, alumina, magnesia, lime, and protoxide of manganese. Its complete analysis may be effected in the following manner:—

The powdered mineral is dissolved by boiling in aqua regia, with effervescence of carbonic acid and separation of silica, with perhaps a little alumina, as an insoluble powder. These are estimated, if necessary, by processes described under the Analysis of Carbonates and of Silicates. The solution, which contains all the bases, with the exception of a little alumina, is evaporated to dryness; the residue is redissolved in dilute hydrochloric acid, and the solution filtered. Unless the solution is very acid, muriate of ammonia is now added, and afterwards an excess of caustic ammonia, which precipitates peroxide of iron and alumina, with small quantities of protoxide of manganese and magnesia. From the solution filtered from this precipitate, *lime* is to be precipitated, as oxalate, by oxalate of ammonia or oxalic acid. The precipitate by ammonia being filtered and washed, is dissolved in a small quantity of hydrochloric acid. This solution is then boiled with excess of caustic potash, to redissolve the *alumina*

at first precipitated by potash, and which is estimated by the usual method. (page 144.) The portion insoluble in excess of potash is dissolved in pure hydrochloric acid, the solution is carefully neutralized with ammonia, and peroxide of *iron* precipitated as succinate or benzoate, with the precautions already described. The filtered liquid, containing small quantities of *magnesia* and protoxide of *manganese*, is mixed with that filtered from the oxalate of lime, and, from the mixture, *manganese* is precipitated as sulphuret, by hydrosulphate of ammonia, and *magnesia* from the filtered solution, as ammonio-phosphate, by phosphate of soda with ammonia. (pp. 318. 331.)

If the amount of iron only is required, the other constituents of the ore being neglected, add ammonia in excess to the solution in aqua regia; after washing, boil the precipitate in solution of caustic potash to dissolve alumina, redissolve the peroxide of iron in hydrochloric acid, and precipitate it again by ammonia: dry, ignite, and weigh.

SECTION IV.

Nickel is weighed best in the state of oxide. It is completely precipitated as oxide by potash from a hot solution, whether ammoniacal salts are present or not. The precipitate, after being washed with hot water, may be ignited and weighed.

Nickel is separated from some substances by precipitation as sulphuret, by hydrosulphate of ammonia in a slightly ammoniacal solution; but as sulphuret of nickel is slightly soluble in that reagent, its complete precipitation is not easily effected. As small an excess as possible of hydrosulphate of ammonia should be employed; the mixture with that reagent should be diluted and exposed in an open vessel to a very gentle heat, that the excess of the hydrosulphate may be

volatilized, or decomposed by the oxygen and carbonic acid of the atmosphere. When the liquid loses its brown colour, the whole of the sulphuret of nickel is precipitated, and may be collected on a filter, and washed with water to which a little hydrosulphate of ammonia has been added. The filter and sulphuret are transferred together to a porcelain capsule, and digested in nitric acid or aqua regia, until the separated sulphur has a pure yellow colour, or is dissolved by the acid; the liquid is then diluted, thrown on a filter, and oxide of nickel is precipitated by potash. The digestion of the sulphuret in nitric acid should not be prolonged, as organic matter from the filter may be dissolved, which will impede the subsequent precipitation of oxide of nickel by an alkali.

Separation of oxide of nickel from peroxide of iron. — These oxides may be separated from each other by either of the processes described for the separation of peroxide of iron from oxide of manganese (page 336.); that is, by means of an alkaline benzoate or succinate, which precipitates peroxide of iron from a neutral solution, but not oxide of nickel; or by boiling carbonate of barytes in a solution of the chlorides of these metals, when peroxide of iron is precipitated, and chloride of nickel remains in solution mixed with chloride of barium. After having filtered the solution of nickel, precipitated the barytes as sulphate, and again filtered, the nickel is precipitated as oxide by potash, then washed, dried, ignited, and weighed.

Separation of nickel from manganese. — 1. These metals are commonly separated by a difficult process, founded on the reducibility of chloride of nickel to the metallic state, when heated to redness, by hydrogen gas, while chloride of manganese resists decomposition under similar circumstances. The reduction may be performed in the apparatus of which a figure is given at page 345. Chloride of manganese may be separated from the resulting metallic nickel by water.

2. M. Ullgren has proposed the following process for the separation of manganese from nickel.* To the solution

* *Rapport Annuel* of Berzelius, 1842, p. 82.

containing these metals is added a mixture of chloride of soda (bleaching liquor) and a caustic alkali, which precipitates each of the metals in the form of peroxide, with the exception of a small quantity of manganese, which remains in solution in the form of hypermanganic acid, and which may be precipitated with ease as peroxide, by boiling the liquid after having added some alcohol or ammonia. The peroxides are collected into a platinum vessel, and dissolved in a weak solution of *pure* hydrofluoric acid. An excess of caustic ammonia is then added to the solution, and the mixture heated nearly to ebullition, on which the whole of the manganese is precipitated as oxide, but the whole of the nickel remains in the ammoniacal solution as a fluoride. The oxide of manganese is then collected on a filter, which should be supported in a silver funnel, and the filtered liquid should be received in a vessel of platinum. The oxide of manganese is ignited and weighed as red oxide, and the ammoniacal liquid is evaporated and mixed with sulphuric acid, to convert the fluoride of nickel into sulphate, from which oxide of nickel is precipitated in the usual manner. Manganese and cobalt may be separated from each other in precisely the same way.

Oxide of nickel may be separated from *alumina* by applying an excess of caustic potash, by which the alumina is dissolved; or by means of sulphite of ammonia, in the same manner as described at page 330. for the separation of oxide of manganese from alumina.

From *magnesia* and the *alkalies*, oxide of nickel is separated by hydrosulphate of ammonia, observing the precautions before mentioned in the precipitation of sulphuret of nickel.

SECTION V.

COBALT.

Cobalt is estimated by precipitating as oxide by caustic potash or soda, and weighing either as oxide or in the me-

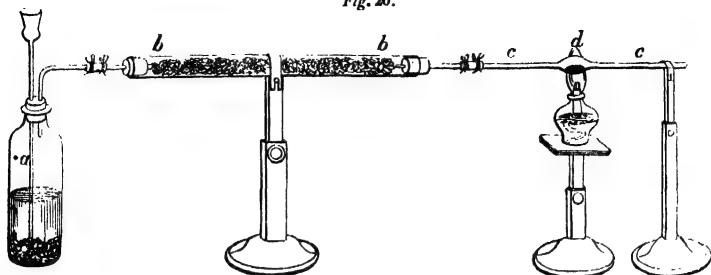
tallic state. The solution containing cobalt should be heated during precipitation, or before it is filtered, and the precipitated oxide washed with hot water and ignited gently. If ammoniacal salts are present in the solution, oxide of cobalt is not precipitated by potash or soda until the salts of ammonia are decomposed by the alkali, and all the ammonia is completely expelled by ebullition. But in such a case, it is better to precipitate cobalt as sulphuret by hydrosulphate of ammonia. To perform this, a slight excess of ammonia is first added to the solution, and then a sufficient quantity of hydrosulphate of ammonia to precipitate the cobalt completely. The precipitated sulphuret is collected on a filter, and washed with water to which a little of the hydrosulphate has been added. When washed, the sulphuret is decomposed by digestion in nitric acid or aqua regia; the solution thus obtained is diluted, and oxide of cobalt precipitated by potash.

The ignition of protoxide of cobalt, previous to weighing, should be performed at a very gentle heat, as it acquires a little oxygen from the air when heated strongly in an open vessel, becoming converted into the peroxide. To avoid this source of error, the protoxide of cobalt may be collected in a weighed filter, placed when washed, together with the filter, in a platinum crucible, and heated in a water-bath so long as it suffers any loss in weight. (See the description of the method of collecting, drying, and weighing a precipitate in a weighed filter, page 15.)

In cases where great accuracy is requisite, instead of weighing cobalt in the state of oxide, it should be weighed in the metallic state, the metal being obtained by reduction of the oxide by heating it strongly in an atmosphere of dry hydrogen gas. This reduction is performed in the apparatus depicted in the annexed figure: *a* is a bottle in which hydrogen gas is generated by the action of dilute sulphuric acid on iron or zinc; as the gas issues from the bottle, it is dried by causing it to pass through the tube *bb*, which contains fragments of dry chloride of calcium. Connected with this chloride of calcium tube is the tube *cc*, having a bulb *d* blown in the middle, into which the oxide

of cobalt for reduction is introduced. This tube should be of hard German glass.

Fig. 20.



Having ascertained the weight of the tube *cc* when empty, the whole of the oxide of cobalt may be introduced into the bulb. As it is difficult, however, to introduce the oxide without loss, it is better to take a part only, and to ascertain the proportion which the amount introduced bears to the entire amount, by the three following weighings:—

1. The entire amount of oxide of cobalt after ignition.
2. The weight of the tube *c* when empty; and,
3. The weight of the tube *c* when the portion of oxide is introduced, from which that of the oxide can be estimated, by deducting the weight of the empty tube.

It may be calculated by the simple rule of proportion what quantity of metal is contained in the whole amount of oxide, when it has been determined, by experiment, what is contained in the portion operated on.

The oxide being introduced, and the apparatus arranged as in the figure, hydrogen gas may be evolved by pouring concentrated sulphuric acid down the funnel of the bottle *a* on zinc and water already in the bottle. After the apparatus is filled with hydrogen, the bulb is heated to *redness** by a spirit lamp. The cobalt is presently reduced from the state of oxide to that of metal, with evolution of heat and light, and production of water. When the decomposition is com-

* Oxide of cobalt may be reduced at a temperature much below redness, but the metallic cobalt thus obtained acts as a pyrophorus when it comes in contact with the air. It does not, however, if heated more strongly.

plete, and the water is expelled by the application of heat along the tube, a current of the gas being still maintained, the bulb is allowed to cool, the tube is disconnected from the apparatus, gently inclined to allow the hydrogen to escape, and then weighed. The weight of the tube when empty being known, the increase is the quantity of metallic cobalt, from which the corresponding quantity of pure protoxide may be obtained by calculation.

Separation of oxide of cobalt from oxide of nickel. — These oxides are not separated from each other without some difficulty. Mr. Phillips has described a process for the purpose, founded on the precipitability of oxide of nickel by potash from an ammoniacal solution of that oxide, while oxide of cobalt remains dissolved. To the solution of these oxides in an acid, a sufficient quantity of muriate of ammonia is added to prevent precipitation by caustic ammonia, which is then applied in excess. The mixture is largely diluted with water which has been recently boiled to expel atmospheric air, and oxide of nickel is precipitated by potash, which alkali is added in sufficient quantity to decompose the ammoniacal salt. The precipitation should be performed in a vessel which can afterwards be closed air-tight. When the oxide of nickel has subsided, it may be collected on a filter, washed with hot water, and weighed; and the oxide of cobalt contained in the filtered solution may be precipitated by hydrosulphate of ammonia. The necessity of avoiding exposure to the air, and of diluting the solution with water deprived of air, arises from the property which the ammoniacal solution of oxide of cobalt possesses, especially if strong, of absorbing oxygen, the protoxide of cobalt being converted into peroxide, which is insoluble in ammonia, and is, consequently, precipitated.

Professor Liebig has recently described a method of separating cobalt and nickel by means of cyanide of potassium. When cyanide of potassium is added to a solution of the salt of nickel, a precipitate of cyanide of nickel is formed, which redissolves on adding an excess of cyanide of potassium, a double compound of cyanide of nickel and cyanide of potassium being formed, which is soluble in water. This

double cyanide is decomposed by dilute sulphuric acid, with precipitation of cyanide of nickel.

When cyanide of potassium and an excess of hydrocyanic acid are added to any salt of cobalt, and the mixture warmed, there is formed the soluble double compound of percyanide of cobalt and cyanide of potassium (cobalti-cyanide of potassium), whose aqueous solution is not at all affected by boiling with hydrochloric, sulphuric, or nitric acid (Gmelin), unlike the analogous compound of cyanide of nickel and cyanide of potassium.

On adding cyanide of potassium in excess to a solution containing nickel and cobalt, with a little free acid, and gently heating, there are formed the double cyanide of nickel and potassium, and the double cyanide of cobalt and potassium. If to this mixture dilute sulphuric acid be added in the cold, three cases present themselves, according to the relative proportions which exist of nickel and cobalt.

(1.) "If the cobalt and nickel in solution are in the proportion of two equivalents of cobalt to three equivalents of nickel (quantities which correspond to their atomic proportions in the cobalti-cyanide of potassium), the precipitate produced is cobalti-cyanide of nickel, and is of a bluish-white colour.

(2.) "If the solution contains less nickel than corresponds to the above proportions" (as would usually be the case in the analysis of an ore of cobalt), "there remains in solution a certain quantity of cobalti-cyanide of potassium, and the precipitate is still cobalti-cyanide of nickel.

(3.) "If there is more nickel present in the solution" (as in the analysis of an ore of nickel), "the precipitate is a mixture of cyanide of nickel and cobalti-cyanide of nickel."*

In the first and second cases, the precipitate produced by dilute sulphuric acid is boiled with the acid fluid until not a trace of hydrocyanic acid is observed to escape (or it may be evaporated nearly to dryness in a water-bath), and then slightly warmed with an excess of carbonate of potash or

* *Philosophical Magazine*, third series, vol. xx. p. 269.

caustic potash; the cobalti-cyanide of nickel is thereby decomposed into pure oxide of nickel, or the carbonate, on the one hand, which is collected on a filter, washed, dried, and weighed; and an alkaline liquid, on the other hand, which contains the whole of the cobalt. The latter is evaporated to dryness, some nitrate of potash being added to it, and the residue ignited. On being afterwards treated with water, the oxide of cobalt remains behind, which may be weighed in the usual manner.

In the third case, which is that of the analysis of nickel ores, having the quantity of cobalt relatively small, it is necessary to add a considerable excess of muriatic acid to precipitate the cyanides dissolved in the cyanide of potassium, and to keep the mixture boiling at least one hour. The precipitate, as first produced, is a mixture of cyanide of nickel and cobalti-cyanide of nickel, but by boiling in hydrochloric acid, the cyanide of nickel is decomposed into chloride of nickel and hydrocyanic acid, the latter being expelled by the ebullition. The cobalti-cyanide of nickel is not affected by the acid. After the acid liquid has been boiled a considerable time, potash is added to the solution, as in the other cases. Chloride of nickel is then decomposed with precipitation of oxide, which falls completely if all the hydrocyanic acid has been expelled by ebullition previous to the addition of the alkali, but not otherwise, as cyanide of potassium would be formed, which is capable of retaining nickel in solution. The cobalti-cyanide of nickel, insoluble in hydrochloric acid, is also decomposed by the potash, with formation of oxide of nickel and an alkaline solution of cobalt. The oxide of nickel is collected on a filter, washed, dried, and weighed; and oxide of cobalt is obtained from the alkaline solution, in the manner above described.

Peroxide of iron may be separated from oxide of cobalt by processes similar to those by which the same oxide is separated from oxide of nickel. The best method is by boiling carbonate of barytes in the solution of the two oxides in hydrochloric acid, when peroxide of iron is precipitated through decomposition of the perchloride of iron, while the

chloride of cobalt is not affected by the earthy carbonate. The peroxide of iron may be dissolved out from the excess of carbonate of barytes by sulphuric acid, and again precipitated by ammonia. From the solution filtered from the peroxide of iron and excess of carbonate of barytes, oxide of cobalt may be precipitated as sulphuret by hydrosulphate of ammonia.

Oxide of cobalt is separated from *alumina* by potash, or by sulphite of ammonia, in the same way as oxide of manganese is separated from alumina, and from *magnesia*, *lime*, and the *alkalies* by hydrosulphate of ammonia.

SECTION VI.

ZINC.

Carbonate of potash and hydrosulphate of ammonia are the reagents generally employed to precipitate zinc from its solutions, for the purpose of weighing; the zinc, in both cases, being afterwards weighed in the state of oxide. When carbonate of potash is used, a sufficient quantity should be added to decompose all ammoniacal salts which may be present, as these prevent the precipitation of subcarbonate of zinc. The mixture should be evaporated to dryness, the residue treated with hot water, boiled and filtered. If no ammoniacal salts are present, the solution may simply be boiled with carbonate of potash and filtered. On ignition, the subcarbonate of zinc loses carbonate acid, and becomes converted into the oxide.

If the zinc is contained in solution as nitrate, unaccompanied by other fixed bases, the most convenient method for its estimation is by evaporating the solution to dryness, and calcining the residuary nitrate of zinc in a platinum crucible at a red heat: The whole of the nitric acid is disengaged, and pure oxide of zinc remains in a fit state to be weighed.

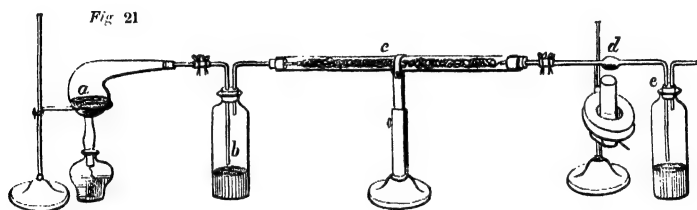
In the form of sulphuret, zinc may be separated from many other bodies by means of hydrosulphate of ammonia, in a neutral or ammoniacal solution. If the solution to be precipitated is acid, caustic ammonia should be added in sufficient quantity to redissolve the precipitate of oxide at first occasioned by the alkali. When hydrosulphate of ammonia has been applied, the sulphuret of zinc which is formed is allowed to subside before filtration, as it would pass through the pores of the paper if the solution were filtered immediately on being precipitated. When the sulphuret has subsided, it may be transferred to the filter (the supernatant liquid being previously decanted), and washed with water to which a little hydrosulphate of ammonia has been added. When washed, it is dissolved in hydrochloric acid without removal from the filter, the solution is boiled to expel sulphuretted hydrogen, filtered, and precipitated by carbonate of potash.

A precaution which should never be neglected in estimating zinc when precipitated as subcarbonate, is to examine whether the liquid filtered from the precipitate contains any more zinc in solution. This is best ascertained by hydrosulphate of ammonia; and the precipitated sulphuret, if any is formed, is converted into subcarbonate, and added to the quantity previously obtained.

Separation of oxide of zinc from oxides of cobalt and nickel.—When the quantity of material operated on is very small (a few grains only), the oxides of cobalt, nickel, and manganese may be separated from oxide of zinc by means of caustic potash. On adding this alkali in excess to a solution of the oxides mentioned in hydrochloric acid, free from ammoniacal salts, oxide of zinc alone is redissolved by the excess, and it may be obtained from the alkaline liquid by neutralizing the latter with an acid, and precipitating by carbonate of potash. Although this method may be practised when the weight of the material does not exceed a few grains, it is impossible to separate the oxide of zinc from the other oxides completely by any excess of potash. When a large amount of the oxides is operated on, another method

is therefore had recourse to. In that generally followed, the chlorides of the metals are formed, and chloride of zinc, which is comparatively volatile, is separated from the other chlorides by distillation.

The first part of the process consists in ascertaining the united weights of the oxides by precipitation from their solution by carbonate of potash, and conversion into oxides by ignition. This being done, the whole or a known proportion of the oxides is then introduced into a bulb blown on a tube of hard German glass, *d* of the annexed figure, and weighed



with the tube. The apparatus being arranged as shown in the figure, the mixed oxides are exposed to the action of a stream of dry hydrochloric acid gas, at the highest temperature procurable by the Rose spirit lamp. The hydrochloric acid is evolved in the retort *a*, from a mixture of chloride of sodium and sulphuric acid; the gas is passed first into the bottle *b*, which contains a little concentrated sulphuric acid, next through the chloride of calcium tube *c*, and then over the oxides in the bulb. By being heated in hydrochloric acid gas, the oxides become converted into chlorides, and the volatile chloride of zinc distils. The exit limb of the bulb tube is bent at right angles about its middle, to enable it to dip into the receiver, which contains water rendered slightly alkaline by ammonia, the surface of the liquid being immediately below the extremity of the tube. When no more chloride of zinc distils, the transmission of hydrochloric acid may be discontinued, the whole of the chloride of zinc which has condensed in the tube near the bulb being previously driven farther on by the application of heat. The part of the tube which contains this portion of chloride of zinc is

divided from the bulb by means of a triangular file, and the chloride is washed into the receiver, the solution in which should now contain all the zinc. From this solution, zinc may be precipitated by carbonate of potash, and weighed as oxide, after being ignited.

The bulb containing the fixed chlorides is weighed, together with the divided portion of the tube, made clean and dry. The difference between the weight of the tube when empty and its present weight is the weight of the fixed chlorides in the bulb. After the weighing, the bulb may be washed out with water, and the cobalt and nickel estimated by the ordinary methods.

Although preferable to the process of separating zinc from cobalt and nickel in which potash is used, the preceding method still does not afford accurate results. The last portions of chloride of zinc which distil over, contain traces of chloride of nickel, and notwithstanding this, the chlorides remaining in the bulb are not entirely free from zinc.

Berzelius has recently made known the following process for separating zinc from cobalt and nickel, which he considers to be very exact. Having first separated the greater part of the oxide of zinc by boiling the mixed oxides in caustic potash, the residue is washed, first with cold and afterwards with boiling water, to withdraw the last traces of potash, ignited, and weighed. After being weighed, the oxides are intimately mixed with finely pulverized sugar, which does not leave an incombustible ash on calcination, the mixture is introduced into a porcelain crucible, and the sugar is carbonized by careful heating. The porcelain crucible is covered, and placed in caustic magnesia contained in an earthen crucible, also covered, and exposed for one hour to the highest temperature of a wind furnace. By this operation the oxides are reduced, zinc is volatilized and completely expelled, and nickel and cobalt remain in the crucible in the state of carburets. The residue in the crucible is treated with nitric acid, to dissolve nickel and cobalt, and the solution is evaporated to dryness in a weighed platinum crucible: on heating the residue to redness, metallic oxides remain, from whose weight

that of the oxide of zinc is calculated, being the loss upon the former weight.*

Another method has been proposed by M. Ullgren. The mixed oxides of zinc, cobalt, and nickel are weighed, and heated to dull redness in an atmosphere of hydrogen, in the apparatus of which a figure is given, page 345. The oxides of cobalt and nickel are reduced to the metallic state by hydrogen, with formation of water, but oxide of zinc remains unaltered. When no more water is produced, the bulb is allowed to cool, the current of hydrogen being still maintained. One of the extremities of the tube *c* is then sealed before the blowpipe, and the tube is filled with a solution of carbonate of ammonia: the open end is corked, and the tube is kept for twenty-four hours at a temperature near 100° Fahr. The oxide of zinc not reduced by the hydrogen dissolves completely in the carbonate of ammonia, from which it may be obtained by evaporating carefully to dryness and igniting the residue; the oxide of zinc remaining is then weighed. The cobalt and nickel are dissolved in nitric acid, and determined by a process already described, page 346.

Separation of oxide of zinc from peroxide of iron. — On adding an excess of ammonia to the solution containing these oxides, the oxide of zinc at first precipitated is redissolved, and a residue of peroxide of iron left. When the proportion of zinc is small compared with that of iron, this process may succeed; but if the zinc is in considerable quantity, no excess of ammonia will separate it completely from the peroxide of iron. In such a case, these oxides are best separated by means of an alkaline benzoate or succinate. (page 339.)

Separation of oxide of zinc from protoxide of manganese. — These oxides may be separated by heating the mixture in an atmosphere of chlorine, in the same manner as practised for the separation of the oxides of cobalt and nickel from oxide of zinc. According to M. Otto, the solubility of the precipitate produced by yellow prussiate of potash with proto-salts of manganese in hydrochloric acid, and the inso-

* *Rapport Annuel* of Berzelius. 2^e Année, p. 81. Paris edition.

lubility in that liquid of the precipitate which yellow prussiate of potash yields with salts of zinc, affords the means of effecting the quantitative separation of these oxides, provided no muriate of ammonia is present in the solution, in which case the precipitate with manganese is as insoluble as that with zinc. When muriate of ammonia is present, the following method may be practised. The solution containing the mixed oxides is supersaturated with ammonia, and then subjected to the action of sulphuretted hydrogen; sulphuret of zinc is first precipitated, and afterwards sulphuret of manganese. When a considerable quantity of sulphuretted hydrogen has been applied, the mixture is supersaturated with acetic acid, which dissolves the sulphuret of manganese, but not the sulphuret of zinc. Both metals are weighed in the state of oxides.

Oxide of zinc may be separated from *lime* by means of oxalate of ammonia in a strongly ammoniacal solution, and from *magnesia* and the *fixed alkalies* by hydrosulphate of ammonia. (page 350.)

SECTION VII.

URANIUM.

Both the peroxide and protoxide of uranium are precipitated from their solutions by ammonia; but as the peroxide is precipitated more completely than the protoxide, it is convenient, when the latter is to be estimated, to convert it into peroxide (uranic acid) by heating with a little nitric acid, before precipitation by ammonia. If the precipitated peroxide, when collected on a filter, is washed with pure water, it passes through the pores of the paper, making the filtered liquid milky: this inconvenience may be avoided, to a great extent, by employing a dilute solution of muriate of ammonia instead of water, in the washing. The precipitate, besides peroxide of uranium, contains ammonia and water, both of which, together with oxygen, it loses on calcination, being

converted into the protoxide of uranium, from the weight of which, that of the peroxide, if the latter was originally present, may be calculated.

If the solution, besides peroxide of uranium, contains a considerable quantity of an earth, the latter is also precipitated by ammonia, in a state of combination with the peroxide, although the earth is one which is not precipitated by ammonia under ordinary circumstances, as lime, magnesia, and barytes. In such a case, when the precipitate is washed, it should be dissolved in hydrochloric acid, and the peroxide reprecipitated by ammonia; the precipitate which then falls is free from the earth, and may be washed with a solution of muriate of ammonia, dried, and calcined. By calcination it becomes the protoxide of uranium, which may be weighed.

Separation of uranium from manganese, nickel, cobalt, and zinc.—According to M. Ebelmen, uranium, in the state of peroxide, may easily be separated from the oxides of manganese, nickel, cobalt, and zinc, by means of a solution of bicarbonate of potash or soda, in which peroxide of uranium is soluble, with the formation of a double uranate and carbonate of potash or soda; but the other oxides mentioned are insoluble in the solution of the alkaline bicarbonate. Caustic potash is added to the solution containing the mixed oxides, and the precipitate produced thereby, after being washed, is digested in a solution of bicarbonate of potash*; or else, the solution is mixed with a slight excess of carbonate of potash (part of which becomes the bicarbonate and dissolves the peroxide of uranium), and the precipitate is collected on a filter, and washed so long as the liquid which passes through is yellow. To separate the peroxide of uranium from either of these solutions, the liquid is saturated with hydrochloric acid, boiled to expel all carbonic acid, and mixed with ammonia to cause the precipitation of peroxide of uranium. The peroxide carries down a small quantity of potash, which is separated by collecting the precipitate, re-

* The presence of phosphoric and arsenic acids does not interfere with this mode of estimating oxide of uranium, but a larger quantity of the caustic and carbonated alkali must then be applied.

dissolving it in hydrochloric acid, and reprecipitating it by ammonia. It may then be collected, converted into protoxide in the usual manner, and weighed. M. Ebelmen considers it advisable to add caustic potash to the solution of the peroxide in the alkaline bicarbonate; after a certain time the whole of the uranium is precipitated as uranate of potash, which is to be washed by affusion and decantation, dissolved in hydrochloric acid, and precipitated by ammonia.

Separation of uranium from iron.—On adding a large excess of carbonate of ammonia to a solution of the peroxides of these metals, the peroxide of uranium at first precipitated is redissolved in the excess, while peroxide of iron remains precipitated. If uranium and iron exist in solution as protoxides, the latter should be converted into peroxides, by heating the solution with nitric acid before carbonate of ammonia is added. The solution of carbonate of ammonia should be considerably diluted before being passed through a filter, else some of the peroxide of iron is also dissolved.

SECTION VIII.

CHROMIUM.

Estimation of chromic acid and oxide of chromium.—Chromic acid may be estimated by precipitation from a neutral solution by protonitrate of mercury; chromate of the suboxide of mercury is precipitated, which may be transferred to a filter and washed. When heated to redness, the precipitate leaves green oxide of chromium, from the weight of which that of the chromic acid may be calculated. According to Rose, chromic acid may be determined more accurately by reducing it to the state of oxide or chloride, by boiling with hydrochloric acid, by which chlorine is liberated. The reduction of chromic acid may be accelerated by the cautious addition of alcohol, any excess of which should afterwards be expelled by evaporation. Oxide of chromium is best precipitated by ammonia; the liquid is

heated gently, filtered, and the precipitate ignited in a covered platinum crucible. By ignition, oxide of chromium is rendered insoluble in acids.

Separation of oxide of chromium from oxide of iron. Analysis of chrome-iron.—The mineral being reduced to a fine powder, is mixed with about three times its weight of fused potash, with the addition of a small quantity of nitre, and the mixture is exposed to a dull red heat in a silver crucible. In this operation the oxide of chromium absorbs oxygen, and becomes converted into chromic acid, which unites with the alkali to form chromate of potash. The fused mass is digested in water until every thing soluble in that liquid is taken up, the alkaline solution is filtered, neutralized with acetic acid, and carbonate of ammonia is added to precipitate *alumina*. After the alumina has been gently ignited and weighed, it should be dissolved in hydrochloric acid to separate a little adhering *silica*, which remains undissolved, and may be collected on a filter, ignited, and weighed. The weight of the silica should be deducted from that of the alumina and silica previously weighed together. The chromic acid existing in the liquid filtered from the precipitate of alumina is reduced to the state of *oxide of chromium* by boiling with hydrochloric acid, the oxide is precipitated by ammonia, filtered, dried, ignited, and weighed. The portion of the fused mass insoluble in water, consisting principally of *peroxide of iron*, is dissolved in hydrochloric acid, the solution is neutralized with ammonia, and peroxide of iron is precipitated by an alkaline succinate or benzoate in the manner described, page 336. If magnesia exists in the ore, as sometimes occurs, it is contained in the liquid filtered from the succinate or benzoate of iron, from which it may be precipitated either as carbonate or ammonio-phosphate. (page 318.)

The following mode of separating oxide of chromium from oxide of iron has been recently proposed by M. Berthier. To the solution containing these oxides, an excess of caustic ammonia or carbonate of ammonia is added, and the resulting precipitate of the hydrated oxides is digested, while still moist,

in a solution of sulphurous acid, which dissolves all the oxide of iron and a little of the oxide of chromium, but the greater part of the oxide of chromium remains undissolved. The solution is boiled until it becomes colourless, when it does not contain a trace of chromium. To estimate the iron in solution, the liquid is boiled with either sulphuric acid or aqua regia to dissipate the sulphurous acid, after which the oxide of iron is precipitated in the usual manner. Or else, the iron may be precipitated by hydrosulphate of ammonia without dissipating the sulphurous acid.

If *alumina* is present, all the oxide of chromium is thrown down completely by merely adding sulphite of ammonia and boiling until the liquid is no longer opalescent. For this purpose, if no alumina, or very little, is present, some alum might be expressly added. If after the subsidence of the precipitate, the liquid retains a green tinge, more sulphite of ammonia and alum should be added, and the boiling be continued. The precipitate, which consists of alumina and oxide of chromium is collected, and dissolved in cold caustic potash. On boiling the alkaline solution the whole of the oxide of chromium is reprecipitated, but the whole of the alumina remains in solution.

SECTION IX.

TITANIUM.

Estimation of titanlic acid. — This acid is best precipitated from its solution by ammonia, as small an excess as possible of that alkali being employed. It is recommended to expel the excess of ammonia, after precipitation, by exposing the liquid to a gentle heat in an open vessel. The precipitate is then transferred to a filter, dried, and ignited. Titanlic acid should be weighed soon after ignition, as it rapidly absorbs moisture from the atmosphere.

Separation of titanlic acid from iron. — The solution of these metals in hydrochloric acid is first neutralized as exactly as possible with ammonia; sulphite of ammonia is then added,

and the mixture is boiled until it is no longer opalescent. The whole of the titanic acid is thereupon precipitated, but the iron remains in solution.

Titanic acid may be separated from *oxides of iron, cobalt, zinc, and manganese*, in the following manner. A considerable quantity of tartaric acid is first added to the solution, which is then supersaturated with caustic ammonia; if sufficient tartaric acid has been previously added, no titanic acid is precipitated by the ammonia. By adding a slight excess of hydrosulphate of ammonia, all the other metals are completely precipitated as sulphurets, leaving in solution titanic acid, which may be obtained by filtering, evaporating the liquid to dryness, and igniting the residue in a platinum crucible until all combustible matter is destroyed. The residue is pure titanic acid, which may be weighed. From *lime* and the *fixed alkalies* titanic acid may be separated by ammonia.

CHAPTER IV.

METALS PROPER, PRECIPITATED BY SULPHURETTED
HYDROGEN FROM THEIR ACID SOLUTIONS.

SECTION I.

LEAD.

Estimation of lead, and modes of separating it from other metals. — Lead may be completely separated from all the metals which have been previously considered, by precipitation as sulphuret, by sulphuretted hydrogen, from a slightly acid solution. If the solution to be precipitated is not already acid, it is best rendered so by the addition of a little nitric acid, as hydrochloric, which is the acid generally used for that purpose with other metals, might cause a precipitate of chloride of lead, which is not decomposed by sulphuretted hydrogen with the same facility as a salt of lead in solution. When the proportion of lead is very small, solution of sulphuretted hydrogen in water may be employed; but in other cases it is better to pass the gas through the solution contained in a bottle having a conical glass stopper. In all cases of precipitation by sulphuretted hydrogen, the gas must be transmitted, or the solution of the gas in water added, until the odour of the reagent becomes very perceptible, and contraction no longer occurs from absorption of the gas above the liquid, when the bottle containing it is agitated. Lead cannot be weighed in the form of the precipitated sulphuret, as it is almost impossible to obtain the latter without an admixture of free sulphur, and it cannot be ignited without decomposition. To obtain the lead in a fit state to be weighed, it is necessary to convert the sulphuret into the sulphate of oxide of lead, which is done in the following manner. After

being collected on a small filter* and washed, the sulphuret is dried and digested, while still in the filter, in a little fuming nitric acid, contained in a weighed platinum capsule, the acid being added very gradually to avoid loss by projection. By this, the sulphuret is entirely converted into sulphate, if the nitric acid is sufficiently strong; if such does not appear to be the case, from some sulphur having been set free without conversion into sulphuric acid, all the nitrate of lead then formed may be converted into sulphate by the addition of a few drops of sulphuric acid. The excess of acid is driven off by evaporation, and the capsule heated to bright redness to destroy the organic matter of the filter. In an open capsule the organic matter burns completely, without any reduction of the sulphate, which is then in a proper state for weighing. From the weight of the sulphate, that of metallic lead or oxide of lead originally present may be calculated.

Lead is also precipitated from its solutions, for estimation, as oxalate, by oxalate of ammonia, as sulphate by sulphuric acid, and as subcarbonate by carbonate of ammonia. In general, Rose gives the preference to oxalate of ammonia. As in the precipitation of oxalate of lime, it is necessary that the solution be neutral, or slightly ammoniacal. After washing and drying the precipitated oxalate, it is removed from the filter, which is burned separately, to avoid any reduction of the oxide by the combustible matter. The ash of the filter is added to the oxalate of lead, which is converted into oxide by ignition, and then weighed.

Sulphuric acid is sometimes used as the precipitant for oxide of lead in the quantitative estimation of that oxide; but in consequence of the slight solubility of sulphate of lead in some saline solutions (see page 91.), this method of estimat-

* It sometimes happens that the sulphuret adheres so strongly to the sides of the vessel in which the precipitation was performed, and also to the tube through which the gas was passed, that it cannot be removed by washing out with water. When this is the case, having first washed out all the adhering liquid, the sulphuret of lead may be readily detached by pouring a few drops of fuming nitric acid on it. Sulphate of lead is then formed, which may be washed out and added to the other quantity of sulphate.

ing lead is often inaccurate. Whenever it is practised the liquid filtered from the sulphate of lead should be tested for lead by sulphuretted hydrogen, and the precipitated sulphuret, if any is formed, be collected and estimated in the usual way.

As caustic potash dissolves oxide of lead, it is sometimes used as the means of separating this oxide from those which are insoluble in potash: after being filtered, the alkaline solution, if it contains no sulphuric acid, should be saturated with acetic acid, and the lead precipitated by oxalate of ammonia. But if any of the lead is present in the form of sulphate, which compound is soluble in solution of potash, the alkaline liquid is evaporated to dryness, the residue treated with an excess of moderately strong sulphuric acid, and the insoluble sulphate of lead collected on a filter. The filtered liquid, diluted with the washings, is treated with sulphuretted hydrogen; and if any sulphuret is precipitated, that is collected and converted into sulphate as usual; or the lead may be precipitated from the alkaline solution as sulphuret, by sulphuretted hydrogen.

From the facility with which compounds of lead are reduced to the metallic state, and an alloy with platinum formed, it is necessary to use porcelain crucibles in the ignition of all lead compounds, except the sulphate.

(For the mode of analyzing sulphuret of lead or common lead ore, and sulphate of lead, see the section headed "Sulphur.")

Analysis of chromate of lead.—The chromate being reduced to a fine powder, it is boiled in hydrochloric acid, with the addition of a little alcohol, when it becomes converted into chloride of chromium, soluble, and chloride of lead, insoluble, in alcohol. The chloride of lead is collected on a weighed filter, washed with dilute alcohol, dried and weighed with the filter, as described at page 15. The alcohol being expelled from the filtered liquid by evaporation, the oxide of chromium is precipitated by ammonia. (See p. 356.)

SECTION II.

CADMIUM.

Cadmium may be separated from all those metals which have been previously considered, with the exception of lead, by passing sulphuretted hydrogen gas into the solution previously rendered slightly acid. If the solution is neutral, hydrochloric acid may be employed to acidify it. The precipitated sulphuret is collected on a filter, washed, and transferred, while still moist and in the filter, into a capsule, and digested with the assistance of a gentle heat in concentrated hydrochloric acid. The sulphuret is thereby decomposed, being converted into chloride of cadmium, with evolution of sulphuretted hydrogen. When the conversion of sulphuret of cadmium into chloride is completed, and the odour of sulphuretted hydrogen no longer perceptible, the solution may be filtered, and cadmium precipitated from it as carbonate, by carbonate of potash. The carbonate is collected on a filter, washed, dried, and heated to redness before being weighed. Ignition reduces carbonate of cadmium to the state of oxide. The filter must be burned separately, as when compounds of lead and some other metals are ignited, oxide of cadmium being easily reduced to the metallic state, and the metal lost from its volatility.

The insolubility of oxide of cadmium in caustic potash affords the means of separating it from *oxide of lead*. (See p. 362.)

SECTION III.

BISMUTH.

By means of sulphuretted hydrogen, bismuth may be separated from all bodies which are not precipitated by that reagent from their solutions in acids. The liquid through

which sulphuretted hydrogen is passed should be diluted; but as the dilution of bismuth solutions by pure water causes the precipitation of subsalts of bismuth, a quantity of acetic acid should be added before dilution. The acetic acid completely prevents precipitation when the liquid is diluted. The solution may now be saturated with sulphuretted hydrogen, and the precipitated sulphuret be filtered, washed, and decomposed by digestion in strong nitric acid: the nitrate of bismuth is thus formed, and sulphur is set free. When the separated sulphur has a pure yellow colour, the sulphuret of bismuth is completely decomposed; the solution is then diluted (a sufficient quantity of free acid being present to prevent precipitation), filtered, the sulphur is washed with water slightly acidified by nitric acid, and oxide of bismuth is precipitated from the solution by carbonate of ammonia. Bismuth is completely precipitated from its solutions by carbonate of ammonia after standing for a few hours in an open vessel, although on first adding an excess of the carbonate, a considerable quantity of the precipitate may be redissolved. The precipitated subcarbonate is ignited in a porcelain crucible, and weighed as oxide. The filter should be burned separately to avoid reduction of the oxide.

When bismuth is to be separated from substances which are not precipitated by carbonate of ammonia, it is unnecessary to convert that metal into the sulphuret, but it may be precipitated at once by the alkaline carbonate. It is absolutely necessary, however, that the solution be free from hydrochloric acid, otherwise the precipitate of subcarbonate will be mixed with an oxichloride of bismuth, which resists decomposition by any excess whatever of the alkaline carbonate. In such a case, the sulphuret of bismuth should first be precipitated by sulphuretted hydrogen, and that decomposed by nitric acid in the manner above described.

Separation of bismuth from lead. — According to Liebig, bismuth may be separated from lead by carbonate of lime, which throws down bismuth, but not lead, from a cold solution of the nitrates of these metals. They may also be separated by adding to the solution in nitric acid, which must be

free from hydrochloric acid, a sufficient excess of caustic potash to redissolve the oxide of lead at first precipitated. (See p. 362.) Oxide of bismuth remains undissolved.

Another method of separating bismuth from lead has been recently described by M. Ullgren. Carbonate of ammonia is added to the solution of the two metals to precipitate the subcarbonates, which are filtered and dissolved in acetic acid. A piece of perfectly pure lead is immersed in the solution, and the containing vessel is carefully closed and set aside for several hours. Metallic bismuth is then precipitated on the lead, an equivalent quantity of the latter being dissolved. When the precipitation is complete, the plate of lead may be separated from the bismuth, washed, dried, and weighed. The precipitated bismuth is collected on a filter, washed with distilled water which has been previously boiled to expel air, and dissolved in nitric acid. The solution of nitrate of bismuth is evaporated to dryness and calcined; pure oxide then remains, which may be weighed. To the solution of lead filtered from the precipitated bismuth, carbonate of ammonia is added, and the precipitate is washed, calcined, and weighed as oxide of lead. By the loss in weight sustained by the metallic lead employed in the process, it is known how much oxide of lead must be deducted from the preceding quantity.*

SECTION IV.

COPPER.

Copper is precipitated from its solutions, for the purpose of estimation, in the state of oxide by caustic potash: the liquid should be rather dilute when precipitated, and always boiled before filtration. In the cold, potash in excess produces with salts of copper a bulky blue precipitate of hydrate of the protoxide, which, on the application of heat, becomes dark brown or black, very dense, and anhydrous. The pre-

* Berzelius, *Rapport Annuel*, 1841. (2^e Année, p. 83. Paris edition.)

precipitate is washed on a filter with hot water, dried, and ignited with the usual precautions to prevent reduction by the combustible matter of the filter. Should a portion of oxide, however, be reduced to the metallic state, it is generally reconverted into oxide by the current of air produced by the combustion of the filter. A portion of the precipitated oxide of copper adheres so tenaciously to the bottom of the vessel in which it was boiled, as not to be removed to the filter without some pains by mechanical means: this, however, is easily effected by dissolving it in a few drops of hydrochloric acid, and reprecipitating the oxide by potash.

Copper is also precipitated for estimation in the metallic state by means of a piece of polished iron; but this method is not admissible in a delicate analysis.

As sulphuret, copper may be separated from many other metals by passing sulphuretted hydrogen gas through the acid solution. The precipitate should be filtered* rapidly, and washed with water impregnated with sulphuretted hydrogen; for when washed with pure water, or water holding air in solution, it oxidizes and dissolves to a small extent, and therefore passes through the filter. When clean, the sulphuret is transferred to a capsule, while still moist and on the filter, and digested in nitric acid or aqua regia, until entirely decomposed; the separated sulphur, if any remains undissolved by the acid, having a pure yellow colour. The solution is diluted, filtered, and decomposed by potash. By the prolonged action of nitric acid or aqua regia on the filter, a soluble organic compound is produced, whose presence impedes the precipitation of oxide of copper by potash, some of the oxide still remaining in solution after an excess of potash has been added. When this is the case (it is perceived by the blue colour of the solution), the portion of oxide must be again precipitated by sulphuretted hydrogen (as the action of this reagent is not affected by the organic matter), and the precipitated sulphuret treated as before. To avoid the incon-

* The sulphuret which adheres tenaciously to the bottle in which the precipitation was effected, and to the tube which conducted the gas, may be detached by means of nitric acid. (See note, page 361.)

venience from the presence of organic matter, the conversion of the sulphuret into nitrate should be effected as expeditiously as possible; or when the greater part of the sulphuret has been disengaged from the filter by the acid, the filter may be removed into another capsule, and the sulphuret remaining attached to it decomposed by a somewhat weaker acid.

The following ingenious mode of determining the amount of copper contained in a solution is easy of execution, and affords results of considerable accuracy when performed with care. It is a modification, by M. Levöl, of a process first contrived by M. Fuchs. The cupreous solution is mixed with a sufficient quantity of caustic ammonia to redissolve the whole of the oxide of copper at first precipitated, introduced into a flask, or, what is more convenient, a large and stout test-tube, which is filled with water which has been recently boiled to expel the dissolved air. A piece of thin and perfectly bright sheet copper, as long and broad as the test-tube will admit, is carefully weighed and introduced into the ammoniacal solution, and the tube is closed perfectly air-tight with a sound cork, well secured.* The tube is then placed in a water-bath, and kept hot until the liquid has lost its blue colour and become colourless, when the piece of sheet copper is quickly removed, washed, dried, and weighed. In this operation, one equivalent of the protoxide of copper (Cu O), dissolved in the ammoniacal liquid, dissolves one equivalent of copper from the sheet copper, to form the suboxide of copper ($\text{Cu}_2 \text{O}$), which is dissolved by the ammonia, forming a colourless solution. Thus the loss in weight of the piece of sheet copper is exactly equal to the weight of the copper in solution to be estimated. The atmosphere must be excluded during the whole process, otherwise the suboxide in solution absorbs oxygen, and becomes protoxide, which of course dissolves more metallic copper.

Separation of copper from lead.—M. Rose recommends the following method for the separation of these metals. Sulphuric acid is added to their solution in nitric acid, and the

* The trouble of corking the tube perfectly air-tight may be avoided by pouring a little oil of turpentine into the tube, so as to form a stratum of about half an inch above the ammoniacal liquid.

mixture is evaporated to dryness, so that the excess of acid may be expelled. On treating the dry mass with water, sulphate of lead remains undissolved, which is collected on a filter, dried, ignited, and weighed. From the filtered solution oxide of copper is precipitated by potash. The alkaline solution filtered from the oxide of copper contains a trace of oxide of lead, dissolved at first by the water as sulphate, and retained in solution afterwards by the excess of potash. In a delicate analysis, this small portion of oxide is worth separating, which is done by first neutralizing nearly the whole excess of alkali by an acid, and then precipitating oxide of lead as oxalate, by oxalate of ammonia.

Separation of copper from zinc: analysis of brass.—Brass may be analyzed in the following manner. The alloy is dissolved in a small quantity of nitric acid, the solution is diluted and treated with sulphuretted hydrogen to precipitate sulphuret of copper, which is converted into oxide in the manner described at page 366., and weighed. From the liquid filtered from the sulphuret of copper, oxide of zinc may be precipitated, after boiling, by carbonate of potash. Or, the zinc may be better estimated by evaporating the solution to dryness, and calcining the residue of nitrate of zinc in a platinum crucible, so as to obtain oxide of zinc, which is weighed. (Page 349.)

Separation of copper from iron, manganese, nickel, and zinc.—Sulphuretted hydrogen is the reagent usually employed for this purpose. When an excess of sulphite of ammonia is added to the solution containing these metals, and the mixture well boiled, the whole of the copper is precipitated as the red sulphite, but all the other metals, according to M. Berthier, remain in solution. The accuracy of this process, however, has been called in question.

Assay of copper ores in the humid way.—The ore, if a carbonate, may be digested in hydrochloric acid, or if a sulphuret, in nitric acid or aqua regia, until the whole of the copper present is dissolved; the greater part of the excess of acid is then expelled by evaporation, and an excess of caustic ammonia is added to precipitate oxide of iron and dissolve the oxide of copper. The precipitate of oxide of iron sometimes

retains a trace of oxide of copper, so minute, however, that it may safely be neglected in an ordinary analysis.

From the ammoniacal solution, the copper may be precipitated as oxide by boiling with caustic potash until the liquid loses all shade of blue; or else the quantity of copper in the ammoniacal solution may be determined by the amount of metallic copper the solution dissolves in forming the suboxide of copper, as above described. When the latter process is followed, it is unnecessary to filter the solution of copper either from the part of the ore insoluble in acids, or from the precipitate of peroxide of iron produced by the addition of ammonia; unless, however, the large bulk of the precipitate renders filtration necessary.

Estimation of the suboxide of copper.—When it is required to estimate the suboxide of copper, the substance to be analyzed should be dissolved in nitric acid. That acid yields oxygen to the suboxide, converting it into the protoxide, which may be precipitated by potash in the usual manner. The amount of suboxide is then calculated from the weight obtained of protoxide.

SECTION V.

SILVER.

Silver may be precipitated from its solutions, and weighed, in the state of chloride, in which form it may be separated from all metals whose chlorides are soluble in water or in dilute nitric or hydrochloric acids. The only metals from which silver cannot easily be separated in this form, are, mercury, when existing as suboxide, and lead, when the latter is in a very large proportion compared with the silver. Either hydrochloric acid, or the chlorides of potassium, sodium, or ammonium, may be employed to precipitate the chloride of silver, but preference is given to the first, as alkaline chlorides exert a slight solvent action on the precipitate. Before precipitation, the solution should be slightly

acidified by nitric acid, and boiled for a few minutes previous to filtering, as the liquid would pass through the filter in a milky state without these precautions. Since chloride of silver is partially reduced by the agency of light, it is proper to keep it in the dark while being filtered: it answers very well to cover the funnel with a piece of blackened paper. When washed and dried, the chloride of silver is removed from the filter into a weighed porcelain crucible, and heated until fusion takes place. The filter is burned separately, its ash being received and calcined in a weighed platinum crucible cover, which is used, after calcining the ash, as the cover for the crucible in which the chloride is fused. From the weight of the chloride of silver, that of the metal or oxide may be calculated. After being weighed, the fused chloride can be easily detached from the crucible, unless the inside of the latter is rough, by digestion in water for a day or two.

Estimation of silver in alloys.—An alloy of silver with other metals may be analyzed by dissolving it in nitric acid, and precipitating silver from the solution as chloride by hydrochloric acid; or, if the alloy is insoluble in nitric acid, it may be treated with aqua regia, when chloride of silver is formed, while the other metals dissolve. A trace of chloride of silver may be dissolved by the acid, but it is precipitated on dilution with water. The chloride of silver may be collected and weighed in the usual manner. From the solution filtered from the chloride of silver, the other metals may be obtained by processes described elsewhere.

Alloys of silver with metals which are oxidable by the air at high temperatures, such as *lead* and *copper*, are analyzed or *assayed* by the process of *cupellation*, which is briefly the following. It consists in fusing the alloy, mixed with a considerable quantity of pure metallic lead, in a small crucible formed of bone earth, which is called the *cupel*. By placing the cupel near an opening in the side of a furnace, air is caused to pass over the surface of the fused metals, which, with the exception of silver, become oxidized; the oxides formed, although by themselves infusible, dissolve in the fused oxide of lead, and are absorbed with it by the porous

cupel, leaving a button of pure metallic silver, which may afterwards be detached and weighed. To ensure accuracy in all cases, this operation requires many precautions, for which I must refer to the "*Traité des Essais par la Voie Sèche*" of M. Berthier, t. ii., and to the article on Assaying in Dr. Ure's Dictionary of Arts and Manufactures.

This operation is practised to a great extent where several such assays are required at the same time; but for a single assay, where the "base" metal is chiefly copper, it is more convenient to dissolve the alloy in pure nitric acid, and precipitate the silver as chloride by dilute hydrochloric acid. When lead is present, a solution of chloride of lead in water may be used as the precipitant of chloride of silver, to avoid the precipitation of any chloride of lead. In cases, however, where the silver is in a very minute proportion, and the great bulk of the alloy is lead, for instance the lead of commerce, in which the proportion of silver varies from three to one hundred ounces per ton, the results obtained in the humid way are unworthy of the smallest reliance. Such an alloy, however, may be cupelled before the blowpipe with ease, after a little practice. The alloy is placed on a dry cupel of bone-earth, and heated with rather a strong oxidizing flame, directed to one side of the melted globule. Two or three times during the operation, the alloy is allowed to cool, and is then removed and beaten in an agate mortar, in order to detach the coating of fused oxide of lead not absorbed by the bone-earth. One hundred grains of the lead alloy is the most convenient quantity to operate upon in this manner: from that amount, every 0.00306 grain of silver obtained, indicates one ounce of silver per ton. (For a minute account of the manner of cupelling silver alloys before the blowpipe, see Plattner's work on the Blowpipe, page 265.)

SECTION VI.

GOLD.

Gold may be separated from most other metals by precipitation in the metallic state from its solution by deoxidizing agents, such as protosulphate or protochloride of iron, proto-nitrate of mercury, oxalic or sulphurous acids. Protosulphate and protochloride of iron are the precipitants generally employed. On adding protochloride of iron to a solution of the chloride of gold, the latter yields all its chlorine to the former, which becomes perchloride of iron, metallic gold being precipitated. A corresponding change occurs when the protosulphate of iron is employed. If a large excess of nitric acid is present in the liquid containing the gold, it should be expelled by evaporation to dryness before adding the salt of iron; the residue is moistened with a little hydrochloric acid, to render it soluble in water, and also to prevent the subsequent deposition of a subsalt of the peroxide of iron on exposure to the air. Protosulphate or protochloride of iron being added, the mixture should be digested for a few hours at a gentle heat, and the precipitated gold filtered, ignited and weighed.

When gold is to be separated from metals, the admixture of iron with which would render their determination difficult, oxalic acid, or an oxalate, is sometimes employed, instead of the proto-salt of iron. The excess of nitric acid in the liquid is first expelled by evaporation, and hydrochloric acid is added to redissolve the residue, and also to prevent the formation of any insoluble oxalates of the metals from which the gold is to be separated. The addition of oxalic acid causes an effervescence of carbonic acid and precipitation of metallic gold; the gold is not, however, completely precipitated without digestion at a moderate heat for a day or two.

From copper, gold may be separated by neutralizing the acid in the solution containing these metals by potash or soda, not ammonia, then adding sulphurous acid and boiling. The gold is deposited in scales, but the copper remains in solution.

Separation of gold from silver.—The analysis of an alloy of gold and silver is one of frequent occurrence. If the proportion of silver is small compared with that of gold, a mass of the alloy is laminated, weighed, and heated with aqua regia, which dissolves the gold completely, leaving a residue of chloride of silver of the form of the alloy operated on. The chloride of silver should be disintegrated with a glass rod, the liquid considerably diluted with water (on which a little more chloride of silver is generally deposited), boiled, filtered, and the chloride of silver weighed. The excess of acid in the filtered liquid being expelled by evaporating to dryness, the residue is diluted, and gold is precipitated from it by oxalic acid. The solution filtered from the gold may then be examined for copper and iron.

If, however, the proportion of silver is large compared with that of gold, the coating of chloride of silver formed by the action of the aqua regia may effectually protect the interior of the alloy from further action, although the latter is reduced to a very thin plate. In such a case, the alloy should be decomposed by boiling in strong nitric acid, the silver being then dissolved, and the gold separated in the form of a powder, which may be collected and weighed. If the alloy resists the action of hot nitric acid, it should be fused with thrice its weight of pure lead, such as that obtained by heating the acetate of lead to redness in a porcelain crucible over a spirit lamp. The lead alloy is readily acted on by nitric acid, all the metals being dissolved except gold, which remains in a pure state, and may be collected on a filter. From the filtered liquid, silver may be precipitated as chloride by a hot solution of chloride of lead.

SECTION VII.

MERCURY.

The most convenient form in which mercury can be obtained fit for weighing, is in that of the metal itself, in which state

it. may also be separated from many other metals. The reducing agent generally employed to obtain metallic mercury from its compounds is protochloride of tin; the reduction of all mercurial salts, whether soluble or insoluble in water and acids (with the single exception of the sulphuret), being easily effected by means of that reagent. When, however, the admixture of tin with the bodies from which mercury is to be separated would render the subsequent determination of the latter difficult, instead of the protochloride of tin, phosphorous acid is employed, which becomes phosphoric acid, when brought into contact with a solution of either of the oxides of mercury, with precipitation of mercury in the metallic state.

If the mercury exists in solution, the routine of the operation is as follows. The liquid is first strongly acidified by hydrochloric acid, an excess of protochloride of tin which has been previously rendered clear by the addition of a few drops of hydrochloric acid is then added, and the mixture is boiled for a few minutes. The boiling should not be continued longer than a few minutes, to avoid the risk of losing mercury by evaporation. When the precipitated mercury is completely deposited, the supernatant liquid should be decanted, and the precipitate boiled with concentrated hydrochloric acid, on which it generally loses its pulverulent appearance, and becomes converted into running globules. If the quantity of mercury is very small, it may be collected in a weighed filter, dried at a temperature not exceeding 120° or 130° Fahr., and weighed with the filter in a covered platinum crucible. (See page 15.) If the quantity of mercury, however, is not small, a better method of collecting it is the following. The precipitate having been boiled in hydrochloric acid (one object of which is to dissolve any peroxide of tin which may have been precipitated), the supernatant liquid is decanted, and the precipitate is washed by affusion of water acidulated with hydrochloric acid, and subsidence. When all the foreign bodies are removed by washing, the humid mercury is allowed to fall into a weighed porcelain capsule, and as much as possible of the

liquid floating over the mercury is taken up by a piece of bibulous paper. The remaining moisture is expelled by evaporation at a temperature not exceeding 150° Fahr. When the mercury is dry, it may be weighed in the porcelain capsule.

If nitric acid exists in the solution from which mercury is to be precipitated, it must be previously expelled by boiling, with the occasional addition of hydrochloric acid, so long as the formation of any chlorine or nitrous acid is perceived from the simultaneous decomposition of nitric and hydrochloric acids. When the quantity of nitric acid is very considerable, it is better first to precipitate the mercury as sulphuret, by means of sulphuretted hydrogen, and then to convert the sulphuret into metallic mercury in the following manner: — The precipitate is collected in a small filter, and introduced, while still moist and on the filter, into a flask containing about one ounce of pure and slightly diluted hydrochloric acid. Through this mixture, chlorine gas is passed, by which the sulphuret is completely decomposed, with formation of chloride of mercury (corrosive sublimate) and free sulphur, some of the latter being slowly converted into sulphuric acid. When the undissolved sulphur is of a pure yellow colour, the transmission of chlorine may be discontinued; the liquid is then boiled to expel free chlorine, filtered, and metallic mercury is precipitated by protochloride of tin.

If the mercurial compound to be analyzed is insoluble, it is introduced, excepting in the case of the sulphurets, into a flask, treated first with strong hydrochloric acid, and then with an excess of a saturated solution of pure protochloride of tin. The mixture is boiled for a few minutes, and allowed to cool, the flask being well corked. When the solution is quite cold, and the decomposition complete, the supernatant liquid may be decanted, and the mercury washed and collected in a porcelain capsule, as described above.

Mercury in solution may be separated from many other bodies by sulphuretted hydrogen: if that reagent precipitates the pure *protosulphuret* (unmixed with free sulphur), the pre-

precipitate may be collected on a weighed filter, dried carefully, and weighed with the filter in a covered platinum crucible, the quantity of metal, protoxide or suboxide, being calculated from the weight of the protosulphuret. If sulphuretted hydrogen precipitates the *subsulphuret*, this compound, as well as the protosulphuret when mixed with free sulphur,—as would occur, if nitric acid, a salt of the peroxide of iron, chromic acid, &c. existed in the solution,—is decomposed by chlorine, in the manner before described, and the resulting chloride of mercury is reduced to metallic mercury, which is weighed. The reason why mercury cannot be well weighed in the state of subsulphuret, is, that a slight elevation of temperature causes the decomposition of the subsulphuret into protosulphuret and metallic mercury, and a portion of the latter might easily be lost, from its volatility.

Separation of the oxides of mercury from the oxide of silver.

—When mercury exists in the state of protoxide (red oxide), it may be separated from silver by first precipitating the latter from the solution, as chloride, by hydrochloric acid; and from the solution filtered from the chloride of silver, metallic mercury is precipitated by protochloride of tin. This method cannot be practised when the mercury is in the state of suboxide (black oxide), as subchloride of mercury would then be precipitated with chloride of silver. In this case, it is necessary to convert the suboxide of mercury into protoxide, by gently heating with a little nitric acid; then to precipitate the silver as chloride; and afterwards, if much nitric acid is present in the solution, mercury should be precipitated as sulphuret, which is converted into chloride by means of chlorine, in the manner before described.

Separation of protoxide of mercury from protoxide of copper.

—If these oxides exist in a dry state, and unmixed with other bodies, their proportions may be determined by expelling the oxide of mercury from a known weight of the mixture by heating to redness in a platinum crucible, and weighing the residuary oxide of copper. If in a state of solution, one method of effecting the separation is the following. The protosulphurets of both metals are preci-

pitated by passing sulphuretted hydrogen gas through the solution, which should not contain free nitric acid, nor any substance capable of precipitating free sulphur. The sulphurets are collected in a weighed filter, washed rapidly, and dried *in vacuo* over sulphuric acid. (page 299.) When dry and weighed, either the whole or a known proportion of the sulphurets is then introduced into a weighed tube retort with an elongated neck, and heated to redness: sulphuret of mercury is thereby volatilized, together with one half of the sulphur contained in the protosulphuret of copper: the latter, therefore, becomes reduced to the state of subsulphuret, which is weighed. Having calculated the quantity of protosulphuret of copper which corresponds to that of the subsulphuret weighed, the amount of sulphuret of mercury may be estimated as loss.

Estimation of mercury in amalgams.—The amount of mercury contained in an amalgam, that is, in an alloy of mercury with other metals, may be determined by ascertaining what loss in weight occurs on volatilizing the mercury by heating the amalgam to redness. If the other metals are not oxidable by the air at high temperatures, a small porcelain crucible may be employed in this operation; but if the metals are oxidable, a tube retort should be used, the neck of which is elongated after the material is introduced, and sealed after the tube has been heated to redness.

By means of sulphuretted hydrogen, mercury in solution may be separated from the metals proper not precipitated by this reagent in their acid solutions, from earths and from alkalies. The precipitated sulphuret of mercury is converted into the chloride by means of chlorine, as described at page 375.; and mercury is precipitated from the chloride in the metallic state by protochloride of tin.

SECTION VIII.

PLATINUM, PALLADIUM, OSMIUM, IRIIDIUM, AND RHODIUM.

Analysis of platinum ore.—The modes by which the metals accompanying native platinum are estimated and separated from each other, are well exhibited in the ordinary process for analyzing platinum ore.

Besides the metals peculiar to the ore, namely, platinum, palladium, osmium, iridium, and rhodium, it contains small quantities of iron and copper. For the method described we are indebted to Berzelius: although an exceedingly complicated process, it is, I believe, the best we possess.

When every thing which seems to be foreign to the ore has been separated by mechanical means, it is digested in dilute hydrochloric acid, in order to remove the metallic iron and peroxide of iron with which the ore is generally mixed; it is then washed, carefully dried, and about thirty grains are weighed out for analysis. After being weighed, the ore is ignited, and dissolved in aqua regia with the assistance of heat, in a glass retort, furnished with a proper receiver, which should be kept constantly cold. When the acid has been distilled so far that the liquid remaining in the retort possesses the consistence of a thick syrup, the mass is dissolved in a very small quantity of water, and the solution carefully poured off from the undissolved residue. The distilled acid, which is yellow, and contains some of the ore projected by the effervescence, is returned to the residue in the retort and redistilled. If the liquid in the receiver is not then obtained in a colourless state it must again be returned to the retort and redistilled.

(A). When procured colourless, the distilled liquid is diluted with water, and ammonia is added to it, so that a slight excess only of free acid remains. To this solution, sulphuretted hydrogen water is added, and the mixture is set aside, out of the contact of air, until the precipitate produced by sulphuretted hydrogen, which is sulphuret of osmium, has completely subsided. The clear supernatant liquid is drawn

off with a syphon, and the sulphuret collected on a weighed filter, washed, dried, and weighed. According to Berzelius, this sulphuret contains between 50 and 52 per cent. of osmium.

(B). If the saline mass in the retort gives a solution smelling of free chlorine when dissolved in water, that odour proceeds from the decomposition of chloride of palladium, and must be expelled by boiling. Should a precipitate appear, it is oxide of palladium; this is redissolved by hydrochloric acid, and the liquid is passed through a weighed filter, to separate some grains of a combination of osmium and iridium, together with some sand which could not be separated before the analysis. When dried, these matters are weighed on the filter without being ignited. If aqua regia containing too much nitric acid is employed to dissolve the ore, peroxide of iridium is occasionally precipitated, which passes through the filter, having the appearance of charcoal.

The filtered liquid is mixed, first, with twice its bulk of alcohol of sp. gr. 0.833, and afterwards with a concentrated aqueous solution of chloride of potassium, which must be added so long as a precipitate appears on agitation.

The precipitate is essentially a mixture of chloride of platinum and potassium, and chloride of iridium and potassium; but it contains, besides these compounds, small quantities of the corresponding double salts of rhodium and palladium. It is collected on a filter, and washed with alcohol of sp. gr. 0.896, to which a little chloride of potassium has been added, till the filtered liquid gives no precipitate with sulphuretted hydrogen water.

The subsequent operations are now divided into two series: first, the treatment of the precipitate; and, secondly, the treatment of the alcoholic solution.

(C). As much as possible of the double chlorides on the filter, when washed and dried, is removed, and carefully mixed with an equal weight of carbonate of soda: the filter, with what remains of the precipitate, being burnt, the ash is mixed with carbonate of soda, and added to the other mixture, and the whole is gently heated in a *porcelain* crucible until it

becomes black throughout. The double chlorides are thus decomposed; the chloride of platinum is reduced to the metallic state, while the iridium and rhodium are oxidized. The saline mass is treated with water, by which the greater part of it is dissolved, and hydrochloric acid is poured on the residue to extract the alkali combined with oxides of iridium and rhodium.

The residue of the action of hydrochloric acid, consisting of metallic platinum and peroxides of iridium and rhodium, is washed, dried, ignited (the filter being burned separately), and weighed. This being done, it is fused in a covered platinum crucible with five or six times its weight of bisulphate of potash, in which the rhodium dissolves, and communicates to it a red colour. This operation is repeated with fresh bisulphate, until the salt no longer acquires a red or pink colour.

(D). The quantity of *rhodium* may be determined in two ways: if the platinum and peroxide of iridium which remain undissolved after fusion with bisulphate of potash are washed, ignited, and weighed, the loss on the weight of the mixture of platinum and peroxides of iridium and rhodium before the fusion indicates *peroxide of rhodium*, which contains 71 per cent. of metal. Or, instead of this method, the saline solution of rhodium may be mixed with an excess of carbonate of soda, evaporated to dryness, and ignited in a platinum crucible: on re-solution in water, peroxide of rhodium remains, which, when washed and dried, is reduced to the metallic state by heating in a tube in a stream of dry hydrogen gas. For the reduction, the apparatus of which a figure is given at page 345. may be employed. The rhodium thus obtained, sometimes contains palladium, which must be extracted by digestion in aqua regia; the acid in the solution is afterwards neutralized by an alkali; and palladium is precipitated as cyanide by cyanide of mercury. On being heated to redness, cyanide of palladium is decomposed into cyanogen gas and metallic palladium, which may be weighed. The weight of this portion of palladium is, of course, deducted from the rhodium.

(E). The next operation is to obtain the amount of *iridium*. The metallic mass which remains after the separation of rhodium by bisulphate of potash is digested with very dilute aqua regia, to remove the greater part of the platinum it contains. The solution thus obtained appears very dark, from the presence of some suspended peroxide of iridium; but when the solid matter has subsided it is of a pure yellow colour, and should then be decanted. The insoluble residue is treated with a mixture of concentrated aqua regia and chloride of sodium, and evaporated to dryness. The use of chloride of sodium is to prevent the formation of protochloride of platinum. When the dry mass is digested in water, peroxide of iridium remains as an insoluble residue, which is filtered and washed, first with a solution of chloride of sodium, and afterwards with muriate of ammonia to remove the common salt. If washed with pure water, the peroxide of iridium would pass through the pores of the filter. It is now burned with the filter, and to be obtained in a fit form for weighing, should be reduced to the metallic state by hydrogen gas, which may be done in the apparatus figured at page 345. A small quantity of iridium exists in the solution of chloride of sodium, to obtain which it is mixed with carbonate of soda, evaporated to dryness, and ignited. The product, when freed from soda salts by water, and from platinum by aqua regia, leaves peroxide of iridium, which is reduced to the metallic state, and added to that already obtained.

(F). Having by these means obtained the weights of the rhodium and iridium, that of the platinum may be calculated. From the united weights of platinum and peroxides of rhodium and iridium (C), subtract the peroxide of rhodium (D), and the iridium (E), (the latter being increased 12 per cent. to convert it into peroxide); the remainder is the weight of the metallic platinum.

Such is one series of operations in this complicated analysis; there still remains for examination the alcoholic liquid filtered from the double chlorides.

(G). This liquid is introduced into a bottle or flask which will permit of being closed air-tight, and a current of sul-

phuretted hydrogen gas is passed through it to saturation. The bottle or flask is then closed, allowed to stand in a warm place for twelve hours, and if the precipitate has subsided, the liquid is filtered, and the alcohol evaporated off. During evaporation, an additional precipitate falls, which is to be added to the former. The precipitate by sulphuretted hydrogen consists of the sulphurets of palladium, rhodium, iridium, and copper; and the liquid filtered from the precipitated sulphurets contains iron, rhodium, and iridium, together with a trace of manganese. During the evaporation of the alcohol, a greasy sulphuret is deposited, which cannot be detached from the sides of the vessel by simple washing, but may be easily removed after all the adhering liquid has been washed away, by dissolving it in ammonia. The ammoniacal solution is evaporated to dryness in a platinum crucible, the residue is mixed with the other sulphurets, and the whole is roasted by heating, with exposure to the air, so long as sulphurous acid is produced. When completely oxidated, the mass is treated with muriatic acid, by which the subsulphates of copper and palladium are dissolved, while oxides of iridium and rhodium, with a trace of platinum, remain undissolved.

(H). To the solution in muriatic acid of the roasted sulphurets of the last operation, a mixture of nitric acid and chloride of potassium is added. On evaporating the mixture to dryness, a dark-coloured saline mass is obtained, which consists of chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium, of which the first two are separated from the third by treatment with alcohol of sp. gr. 0.833, in which the former dissolve, leaving the double salt of palladium as an insoluble residue, which is collected on a filter and washed with alcohol. When dried and ignited, this salt may be weighed: it contains 28.84 per cent. of palladium. The alcoholic solution filtered from the palladium salt is concentrated by evaporation, and oxide of copper precipitated from it by potash. (page 365.)

(I). The portion of the roasted sulphurets (G) insoluble in hydrochloric acid, consisting of oxides of iridium and

rhodium, with a trace of platinum, is fused with bisulphate of potash in a platinum crucible to dissolve out the rhodium; an operation which is repeated until the bisulphate no longer acquires a red or pink colour. The rhodium is determined by one of the methods before described. (D). The residue undissolved by bisulphate of potash, which is peroxide of iridium with a little platinum, is treated with aqua regia, and the peroxide reduced by hydrogen gas, in the same manner as described in a previous part of the analysis. (E).

(K). The concentrated solution from which the sulphurets were precipitated contains a small quantity of iridium and rhodium, protochloride of iron, and a trace of manganese. The quantity of the last is commonly too minute to be determined. The iron is peroxidized by heating with nitric acid, and weighed as peroxide, obtained by precipitation by ammonia. But this peroxide of iron contains a small quantity of a combination of iridium and rhodium, to separate which, after weighing the peroxide, it must be reduced by hydrogen gas: the reduced metal is treated with hydrochloric acid to dissolve iron, and the black undissolved portion is collected on a filter, ignited with exposure to the air, and weighed; its weight, deducted from that of the peroxide of iron previously obtained, leaves the quantity of the latter in a pure state.

The solution filtered from the precipitate by ammonia is mixed with carbonate of soda in sufficient quantity to decompose the ammoniacal salts, and evaporated to dryness. On treating the residue with water after a gentle ignition, peroxides of iridium and rhodium remain undissolved, but the amounts of these are in general too small for separation.

To facilitate the conception of this intricate analysis, I have annexed the following tabular view of the several steps in the process.

The weighed ore is dissolved in aqua regia, distilling the acid:

- (a). The distilled liquid contains *osmium*; dilute with water, neutralize most of the excess of acid by

ammonia, and precipitate osmium, as sulphuret, by sulphuretted hydrogen; weigh the sulphuret of osmium.

- (b). Dilute the concentrated solution in the retort, and collect the undissolved grains of osmium and iridium (with sand) in a weighed filter; weigh this insoluble matter.

Mix the filtered solution with twice its bulk of alcohol of sp. gr. 0.833, and chloride of potassium, filter, and wash with alcohol.

The operation is now divided into, I., the examination of the precipitate; and, II., the examination of the alcoholic solution.

I. EXAMINATION OF THE PRECIPITATE PRODUCED BY CHLORIDE OF POTASSIUM.

The precipitate consists of the double chloride of platinum and potassium, the double chloride of iridium and potassium, and the double chloride of rhodium and potassium. Mix it with carbonate of soda, and ignite the mixture in a porcelain crucible; treat the ignited mass first with water, and afterwards with dilute hydrochloric acid. Wash, dry, and weigh the insoluble residue of metallic platinum and peroxides of rhodium and iridium, and after weighing fuse it with bisulphate of potash.

Platinum and peroxide of iridium remain undissolved by the bisulphate. Treat the saline mass with water, and wash, ignite, and weigh the insoluble residue. When weighed, digest the residue in aqua regia with the addition of some chloride of sodium.

Rhodium is dissolved in the bisulphate, and may be separated from the insoluble residue by treating the mass with water. Having weighed the residue, the quantity of rhodium may be determined from the loss on the weight of the mixture of platinum and peroxides of rhodium and iridium, before fusion with bisulphate of potash. The loss is *peroxide of rhodium*.

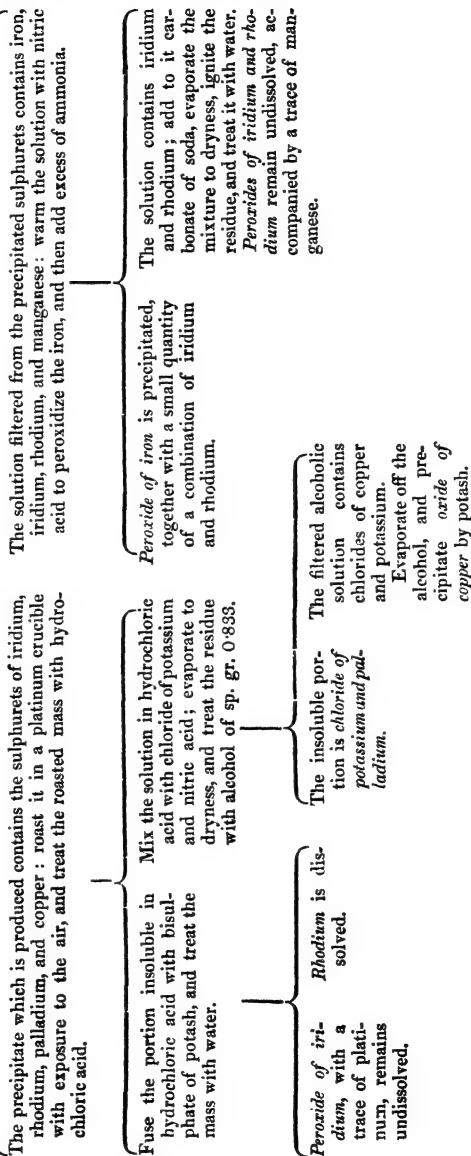
The portion undissolved is *peroxide of iridium*, which is reduced to the metallic state by hydrogen gas, and weighed.

The solution in aqua regia contains platinum and a little iridium: add to it carbonate of soda, evaporate the mixture to dryness, and ignite the residue: treat the ignited mass first with water, and afterwards with aqua regia.

Peroxide of iridium remains undissolved: it should be reduced to the metallic state by hydrogen gas, and weighed. The weight of *platinum* is known by deducting the united weights of the peroxides of iridium and rhodium from the weight of the mixture of these with metallic platinum previously ascertained.

II. EXAMINATION OF THE ALCOHOLIC SOLUTION FILTERED FROM THE PRECIPITATE PRODUCED BY CHLORIDE OF POTASSIUM.

Transmit sulphuretted hydrogen gas in excess through the solution, and allow the liquid to remain in a warm place for twelve hours.



Separation of platinum from gold. — The alloy of these metals is dissolved in aqua regia; gold is precipitated in the metallic state by adding oxalic acid and boiling; (see page 372.) and from the filtered solution platinum is precipitated in the metallic state by the addition of formic acid. Or, the solution of these metals may be mixed with sulphurous acid and boiled, on which the gold is precipitated in scales, but the platinum remains in solution. (M. Berthier.)

SECTION IX.

TIN.

Tin is best weighed in the state of peroxide. If the metal is contained in solution in the state of *protoxide*, or *protochloride*, strong nitric acid should be added to the solution, and the mixture evaporated nearly to dryness at a boiling heat; the protoxide of tin is thereby converted into the insoluble peroxide. Although peroxide of tin is insoluble in nitric acid, after being boiled in the liquid, it is still slightly soluble in hydrochloric acid. If the latter acid is present, therefore, it should be expelled from the liquid by boiling, with the occasional addition of some nitric acid; the hydrochloric and nitric acids suffer mutual decomposition, with the formation of nitrous acid and free chlorine, both of which are expelled by the ebullition. When the conversion of protoxide into peroxide of tin is complete, which is perceived by the cessation of nitrous vapours, the liquid may be diluted with water, and the peroxide collected on a filter. Peroxide of tin must be ignited previous to being weighed.

If tin exists in solution in the state of *peroxide*, or *perchloride*, the solution is boiled with nitric acid in the same manner; peroxide of tin is thus precipitated, which may be filtered, ignited, and weighed.

If the substance of which the tin is an element is a metallic alloy, it should be boiled in moderately strong nitric acid, when the oxides of all metals which are soluble in that acid are formed and dissolved, while the tin is converted

into insoluble peroxide. The liquid is evaporated until nearly all the excess of acid is expelled, diluted with water, and filtered to collect the peroxide of tin, which is ignited and weighed.

As tin is precipitable by sulphuretted hydrogen, whether existing in the state of protoxide or peroxide, that reagent affords the means of separating tin from the alkalies, earths, and the metals not precipitated by sulphuretted hydrogen from their acid solutions. To estimate tin in such a case, the precipitated sulphuret, when washed and dried, is introduced into a flask, and treated with fuming nitric acid, proper means being adopted to prevent loss of the solution by projection, from the intensity of the action. The tin is thus converted into peroxide, and the sulphur into sulphuric acid. The acid liquid is poured into a platinum capsule or crucible, and evaporated carefully to dryness. When all the nitric and sulphuric acids are expelled, the residue should be heated to redness, after which, pure peroxide of tin remains. In case a little sulphuric acid should be retained by the peroxide, it is recommended, after the first weighing, to place a fragment of carbonate of ammonia in the crucible, and to heat again to redness, and weigh.

The *analysis of the native oxide of tin* is performed in the following manner:—Mix the finely powdered ore with five or six times its weight of caustic potash or soda, heat the mixture to dull redness in a closely covered silver crucible for half an hour, and dissolve the resulting mass, which is usually green, in hydrochloric acid. Evaporate off most of the excess of acid, dilute the remaining liquid with water, and precipitate tin as sulphuret by sulphuretted hydrogen. Treat the precipitated sulphuret of tin with fuming nitric acid in the manner before described. The liquid filtered from the sulphuret contains protochloride of iron; peroxidize the iron by boiling the solution with nitric acid, neutralize with ammonia, and precipitate peroxide of iron by a neutral alkaline benzoate or succinate. (page 336.) From the liquid filtered from the precipitate of benzoate or succinate of iron, manganese may generally be precipitated by hydrosulphate of ammonia.

SECTION X.

ANTIMONY.

For the estimation of antimony, that metal is best precipitated as sulphuret, from its slightly acidified solutions, by means of sulphuretted hydrogen. It is indifferent, in this operation, whether the antimony exists in the state of oxide or the corresponding chloride, or as antimonious or antimonie acid. Before applying sulphuretted hydrogen gas, the liquid should be diluted with water; but if the solution is neutral, or nearly so, dilution with water may cause the precipitation of a subsalt of antimony, an inconvenience that is avoided by first adding a considerable quantity of tartaric acid to the solution, after which it may be diluted with water, without the production of any precipitate. The liquid, when saturated with sulphuretted hydrogen, should be left in a warm place exposed to the air, until the odour of the gas entirely disappears. The necessity of getting rid of the excess of sulphuretted hydrogen arises from the circumstance that water saturated with that gas possesses the property of retaining considerable traces of sulphuret of antimony in solution, which are deposited, however, when the sulphuretted hydrogen is dissipated.

The precipitated sulphuret is collected on a weighed filter, dried, and weighed with the filter in the usual manner. If the precipitate which is weighed is the pure sulphuret of antimony (Sb S_3) corresponding to the oxide of antimony (Sb O_3), we can, from its weight, calculate at once the amount of metal or oxide it represents. But that sulphuret is rarely precipitated in a state of sufficient purity for the calculation, it being generally contaminated with free sulphur, and sometimes with the higher sulphurets of antimony, namely, those corresponding to antimonious and antimonie acids, when it is obviously impossible to estimate, from the weight of the sulphuret, the amount of the metal it contains. To ascertain, therefore, the purity of the precipitated sulphuret, after having weighed it, digest a small por-

tion in concentrated hydrochloric acid: if it dissolves completely, with evolution of sulphuretted hydrogen, it is the pure sulphuret corresponding to the oxide; but if it leaves sulphur undissolved, it contains either free sulphur or a higher sulphuret of antimony. In the latter case, it is necessary that another operation should be performed to ascertain the real amount of antimony contained in the sulphuret. A known weight is introduced into a flask, and fuming nitric acid is added, drop by drop, proper means being taken to prevent loss of the liquid by projection. When a considerable quantity of nitric acid has been thus gradually added, hydrochloric acid is applied, and the mixture is digested at a gentle heat until the whole or the principal portion of the sulphur is dissolved. The liquid is diluted and the undissolved sulphur, if any remains, is collected in a weighed filter, dried carefully and weighed on the filter in the ordinary manner. The sulphuric acid into which the remainder of the sulphur has been converted is precipitated by chloride of barium, after an addition of tartaric acid, to prevent the precipitation of a subsalt of antimony, on dilution with water. From the weight of the precipitated sulphate of barytes, that of the sulphur it contains is calculated, which, added to that already weighed, and the sum deducted from the weight of the sulphuret of antimony employed, leaves the amount of metallic antimony in the sulphuret. Another calculation is then necessary to ascertain how much antimony was contained in the entire amount of the sulphuret precipitated by sulphuretted hydrogen, as a portion of it only was operated on.

Separation of antimony from other metals.—From those metals whose sulphurets are insoluble in hydrosulphate of ammonia, (*manganese, iron, zinc, cadmium, cobalt, lead, bismuth, silver, and mercury,*) antimony may be separated by the ready solubility of its sulphuret in that liquid. The metallic alloy, or mixture of oxides, is dissolved in concentrated hydrochloric acid or aqua regia, and the solution is supersaturated, first with ammonia, and afterwards with an excess of hydrosulphate of ammonia, which should contain

its full dose of sulphur. After a gentle heating, the liquid is filtered, and the precipitate is washed with water to which some hydrosulphate of ammonia has been added. The filtered liquid is a solution of sulphuret of antimony in hydrosulphate of ammonia; and the former may be precipitated by the addition of acetic acid, of which a slight excess should be used. The quantity of antimony in the precipitate is then determined by the process before described.

In an alloy, antimony may be separated from many other metals by a process founded on the volatility of its chloride. The alloy, reduced to a state of powder, is introduced into the bulb of the tube *d* of the apparatus figured at page 351., and chlorine gas is caused to pass through the tube. The wash-bottle *b* may contain water to arrest hydrochloric acid. The bottle *e* is one half or two thirds filled with a weak solution of tartaric acid, to which a little hydrochloric acid is added. When the apparatus is full of chlorine, heat should be applied to the bulb; chloride of antimony then distils into the receiver, affording a limpid solution, if sufficient tartaric and hydrochloric acids are present. When all the chloride of antimony is distilled, the tube is divided near the bulb, and the adhering chloride of antimony is washed into the receiver. Through the solution thus obtained, sulphuretted hydrogen gas is passed, to precipitate antimony as sulphuret, and the purity of the precipitate is tested in the manner before described. The quantity of the fixed chlorides in the bulb may be estimated by first weighing the tube in its present state, then dissolving out the chlorides by water or an acid; and, lastly, weighing the empty tube when cleaned and dried. The difference in the two weighings is, of course, the weight of the fixed chlorides.

Separation of antimony from tin.—From tin, the sulphurets of which metal are soluble in hydrosulphate of ammonia, antimony may be separated by precipitating it in the metallic state from the solution of the two chlorides by a bar of tin with the assistance of heat. The precipitated antimony may be collected, dried, and weighed; and the

united weights of the two metals being previously ascertained, the amount of tin originally present is known from the loss. If the metals exist in solution, and their united weight is not known, they may both be precipitated together in the metallic state by a bar of zinc: after being collected and weighed, the mixed metals are dissolved in hydrochloric acid with a few drops of nitric acid. Metallic antimony may then be precipitated by tin, collected on a weighed filter, dried, and weighed.

Estimation of antimonie acid. — If the antimonie acid is dissolved in an alkaline liquid, the excess of alkali is first neutralized by adding nitric acid until a precipitate begins to appear. Antimonie acid is then precipitated in the form of the antimoniate of the suboxide of mercury, by adding a solution of the protonitrate of mercury. A few drops of ammonia may be added to the mixture, to ensure the complete precipitation of the antimoniate. The precipitate is collected, dried, and heated to redness. By ignition, it is decomposed, oxide of mercury being given off, and pure antimonie acid remaining, in a fit state to be weighed.

SECTION XI.

MOLYBDENUM.

To estimate molybdenum, or molybdic acid, the concentrated solution of the substance is treated with an excess of hydrosulphate of ammonia; the sulphuret of molybdenum is thus formed, and is dissolved by the excess of hydrosulphate. From the solution, when diluted, the tersulphuret of molybdenum is precipitated by adding hydrochloric or acetic acid, and the mixture is digested at a gentle heat, until the odour of sulphuretted hydrogen is no longer perceptible. The precipitated tersulphuret, when calcined in a small retort, parts with sulphur, being converted into the grey bisulphuret, in which state it is weighed. From the weight of the sul-

phuret, the amount of molybdenum it contains, or molybdic acid it represents, may be estimated.

Analysis of molybdate of lead.—Dissolve the powdered mineral in dilute hydrochloric acid, with the assistance of heat, and collect the chloride of lead which is formed in a weighed filter; after washing with water, and drying, weigh the chloride in the filter with the usual precautions; neutralize the filtered liquid by ammonia, add an excess of hydrosulphate of ammonia, and digest the mixture for an hour in a closed flask. The lead not precipitated as chloride now falls as sulphuret, which may be collected and estimated by conversion into sulphate of lead. (page 360.) To the liquid filtered from the sulphuret of lead, which is a solution of sulphuret of molybdenum in hydrosulphate of ammonia, add hydrochloric or acetic acid, and allow the mixture to digest at a gentle heat until the odour of sulphuretted hydrogen is no longer perceived. Calcine the precipitated tersulphuret of molybdenum, when dry, in a small retort, and weigh it as the bisulphuret.

SECTION XII.

TUNGSTEN.

Estimation of tungstic acid.—The ordinary process for estimating tungstic acid in a solution resembles that by which molybdic acid is estimated. An excess of hydrosulphate of ammonia is added to a concentrated neutral or alkaline solution containing the tungstic acid; sulphuret of tungsten is thus formed, and is dissolved in the excess of hydrosulphate of ammonia. The sulphuret in solution is now precipitated by dilute nitric acid, and the mixture is exposed to a gentle heat to expel the excess of sulphuretted hydrogen, on which all the tungsten is precipitated as tersulphuret, of a yellow colour. The precipitate is collected on a filter, washed with water slightly acidified by hydrochloric acid, dried, and ignited strongly in a platinum crucible with exposure to the

air. The sulphuret thereby becomes oxidized and converted into tungstic acid, whose weight may be determined. When tungstic acid exists in solution, with no other base but ammonia present, its weight may be determined by evaporating the solution to dryness, and calcining the residue, after which pure tungstic acid remains.

Tungstic acid may be precipitated from its solution, for the purpose of weighing, by means of protonitrate of mercury, in precisely the same manner as antimoniac acid. (See *Estimation of antimoniac acid*, p. 392.)

Analysis of tungstate of lime.—The analysis of tungstate of lime may be performed in the following manner:—The mineral is reduced to a fine powder, and digested at a gentle heat in three times its weight of concentrated nitric acid until nearly all the acid is evaporated. If the digestion and evaporation are repeated, the tungstate of lime is entirely converted into nitrate of lime, and the tungstic acid is set at liberty. When the excess of nitric acid is evaporated off, alcohol is added to the dry mass to dissolve nitrate of lime, and the residue, which is tungstic acid, is dissolved in ammonia. If any thing remains undissolved after the successive action of alcohol and ammonia, it is probably silica or some stony matter foreign to the mineral. To estimate the lime, sulphate of ammonia is added to the alcoholic solution to precipitate sulphate of lime, which is dried, ignited, and weighed. The solution of tungstic acid in ammonia, when evaporated to dryness and calcined, leaves pure tungstic acid.

Analysis of Wolfram (tungstate of iron and manganese).—The finely powdered mineral is fused in a platinum crucible with twice its weight of carbonate of soda, and the fused mass is digested in water until nothing more is dissolved by that liquid. On treating the residue insoluble in water with hydrochloric acid, oxides of iron and manganese dissolve; these oxides are separated from each other by an alkaline succinate or benzoate. (p. 336.) From the alkaline solution of the fused mass in water, tungstic acid is precipitated by hydrochloric acid, washed, and redissolved in solution of ammonia. On evaporating this solution to dryness, and

calcining the residue, pure tungstic acid remains, which may be weighed. Or, instead of that, the tungstic acid may be precipitated by protonitrate of mercury, when the tungstate of the suboxide of mercury falls, which leaves a residue of pure tungstic acid, when heated to redness, in a fit state for being weighed.

SECTION XIII.

ARSENIC.

Estimation of arsenic in alloys, arseniurets, arsenites, and arseniates.—To estimate arsenic, the solution in an acid of the substance to be analyzed should be diluted with water, and the arsenic precipitated from it as sulphuret by sulphuretted hydrogen. The precipitated sulphuret is that which corresponds to the degree of oxidation of arsenic in the solution: if the arsenic in solution is in the state of arsenious acid, then sulpharsenious acid is precipitated; but if as arsenic acid, it is sulpharsenic acid which is formed. Frequently the precipitate consists of a mixture of the two sulphurets. When the subject of analysis is an arseniuret, that is, a combination of arsenic with another metal, it should be dissolved by aqua regia: the whole of the arsenic is then converted into arsenic acid. If the compound for analysis is a soluble arsenite or arseniate, it should be dissolved in water, and the solution acidified strongly by hydrochloric acid before applying the gas. As a solution of arsenious acid is precipitated by sulphuretted hydrogen with greater facility than a solution of arsenic acid, it is advisable to reduce arsenic acid to the state of arsenious acid, before exposing it to sulphuretted hydrogen. This may be effected by means of sulphurous acid at a boiling heat. (See p. 282.)

When saturated with sulphuretted hydrogen, the liquid should be gently heated in an open vessel until the excess of the gas is dissipated, as the aqueous solution of sulphuretted hydrogen is capable of dissolving a small quantity of the sulphurets of arsenic.

If no doubts of the purity of the precipitate are entertained, that is, of its containing no free sulphur, and of its being either entirely sulpharsenious or sulpharsenic acid, and not a mixture of these sulphurets, then it may be collected in a weighed filter, dried, and weighed with the filter, and from the weight of the sulphuret, the quantity of metallic arsenic it contains, or arsenious or arsenic acid it represents, may be deduced by calculation. But it rarely happens that the sulphuret is obtained sufficiently pure for the calculation: for as the mere exposure of solution of sulphuretted hydrogen to the air causes a precipitate of sulphur, it is scarcely possible to obtain either of the sulphurets quite free from that element. Another operation must then be performed to ascertain the true amount of arsenic in the precipitate, which is precisely analogous to that already described for a similar purpose under antimony. (page 389.) After the sulphuret is collected on a weighed filter, washed and dried, it is weighed together with the filter, and as much as can easily be removed is introduced into a flask, and digested with aqua regia. The remaining sulphuret with the filter is weighed, after another drying, to know the amount introduced into the flask. By digestion with aqua regia, the arsenic becomes converted into arsenic acid, and a portion or the whole of the sulphur into sulphuric acid. After a long digestion, to ensure perfect decomposition of the sulphuret, the liquid is diluted, and the undissolved sulphur (if any) is collected in a weighed filter, dried and weighed. The sulphuric acid in the solution is estimated as sulphate of barytes, the liquid being made pretty strongly acid to prevent the precipitation of arseniate of barytes. The sulphate of barytes being weighed, the quantity of sulphuret it contains is calculated, and added to that already collected: the sum, deducted from the weight of the sulphuret employed, leaves the amount of metallic arsenic.

After having precipitated arsenic in the state of sulphuret from a solution of arsenious acid, by means of sulphuretted hydrogen, and determined the weight of the precipitate, the small quantity of free sulphur which is mixed with it may often be perfectly separated by treating the precipitate with

ammonia, which dissolves the sulphuret of arsenic without affecting the sulphur. The quantity of sulphur can then be readily determined. (Rose.)

In this manner the acids of arsenic may be separated from the *alkalies*, *earths*, and all metals not precipitated by sulphuretted hydrogen from their acid solutions.* From the greater number of those metals the solutions of which are precipitated by sulphuretted hydrogen, arsenic, like antimony, may be separated by the ready solubility of its sulphurets in hydrosulphate of ammonia. To the solution of the substance, add first an excess of pure ammonia, and afterwards an excess of hydrosulphate of ammonia; sulphurets of the various metals are thereby formed, sulphuret of arsenic is redissolved, while the other sulphurets remain insoluble. When cold, the precipitate is collected on a filter, and washed with water containing a little hydrosulphate of ammonia. On acidifying the filtered liquid with acetic acid, sulphuret of arsenic and free sulphur are precipitated, and sulphuretted hydrogen is evolved. After the liquid has been digested at a gentle heat until the odour of sulphuretted hydrogen is no longer perceptible, the precipitate may be collected on a weighed filter, and its proportion of arsenic determined by one of the processes above described.

Alloys of arsenic with metals whose chlorides are not volatile at a red heat, may be analyzed by exposing the alloy to chlorine gas, and distilling the volatile chloride of arsenic in precisely the same manner as the chloride of antimony in the analogous method of analyzing alloys of antimony.

Separation of arsenic from antimony.—The common method of separating arsenic from antimony is not very exact. If the substance for analysis is an alloy consisting of no other metal than arsenic and antimony, the former may be separated

* It has been observed by M. Wöhler, that when sulphuretted hydrogen gas is passed through a solution in a mineral acid of arsenic acid and oxide of zinc, the precipitate which is produced is a combination of sulpharsenic acid and sulphuret of zinc ($ZnS + AsS_3$), whatever excess of free acid may exist in the solution. But if the arsenic acid is reduced to the state of arsenious acid before transmitting sulphuretted hydrogen (which may be effected by means of sulphurous acid, page 282.), sulpharsenious acid is precipitated in a pure state, all the zinc remaining in solution.

from the latter by distillation in an atmosphere of hydrogen gas. The alloy is powdered and introduced in the bulb of the tube (*fig.* 20. p. 345.); dry hydrogen gas is passed through the apparatus, and the heat of a spirit lamp is applied to the bulb until all the arsenic is distilled and driven out of the tube. The weight of the residue of metallic antimony deducted from the original weight of the alloy gives that of the arsenic expelled.

When arsenic and antimony occur mixed with other metals, or in a state of solution, the above process cannot be practised. In such a case, the solution of the substance (previously mixed with tartaric acid to prevent the precipitation of a subsalt of antimony) is diluted with water, and the sulphurets of both metals are precipitated by sulphuretted hydrogen. The two sulphurets should be well mixed by agitation, and then collected in a weighed filter, washed, dried, and weighed. Two operations are now to be performed on the precipitate; the first to ascertain its amount of sulphur, and the second to ascertain the relative proportions of antimony and arsenic present. 1. The weight of the whole precipitate being ascertained, about one half of it is removed into a flask, and the filter with the remainder is warmed and weighed, to learn the quantity introduced into the flask. That portion is very cautiously treated with aqua regia, beginning by adding fuming nitric acid, drop by drop, and afterwards adding hydrochloric acid with the same caution. Tartaric acid is added to the solution thus formed, which is diluted with water, and any sulphur which may remain undissolved is collected and weighed. The sulphuric acid in solution is then estimated as sulphate of barytes, the proportion of sulphur in which, added to that previously weighed, and the sum deducted from the weight of the sulphurets employed, gives the proportion of mixed antimony and arsenic. 2. To obtain the relative proportions of the two metals, a known weight of the other portion of the precipitated sulphurets is heated in a current of hydrogen gas in the apparatus (*fig.* 20. p. 345.), when sulphur from the sulphuret of antimony is first disengaged, and afterwards

sulphuret of arsenic sublimes, leaving a residue of metallic antimony, which may be weighed. Having previously obtained the united weight of both metals, the weight of the arsenic can now be calculated. When arsenic and antimony are mixed with metals which are precipitated by sulphuretted hydrogen from their acid solutions, but whose sulphurets are insoluble in hydrosulphate of ammonia, the two sulphurets may be obtained together, separate from the other sulphurets, in the same manner as arsenic or antimony alone is separated from such metals.

The following method of separating antimony from arsenic has been recently proposed by M. Behrens. The two metals are precipitated from their solution as sulphurets by sulphuretted hydrogen; the sulphurets are collected, mixed with an equal bulk of nitrate of lead and as much water, and the mixture is boiled with constant stirring and addition of water to compensate for that which evaporates, until it becomes dark brown. The undissolved portion contains the whole of the antimony and some of the arsenic in the state of a double sulphuret of arsenic and lead.

To the solution, which contains arsenic, nitrate of lead, and free nitric acid, carbonate of ammonia is added so long as a precipitate of carbonate of lead is produced; the solution is separated by filtration from the carbonate of lead, acidified by hydrochloric acid, and then treated with sulphuretted hydrogen to throw down the arsenic as sulphuret.

The insoluble mass containing the antimony and a portion of the arsenic is digested in ammonia, which is said to dissolve only sulphuret of arsenic: the solution is filtered, mixed with hydrochloric acid, and the precipitated sulphuret of arsenic added to that before obtained. The antimony, which remains undissolved, may be separated from the lead and estimated in the usual manner. (page 390.)

CHAPTER V.

NON-METALLIC BODIES.

SECTION I.

SILICON.

Estimation of silicic acid (silica).—For the purpose of estimation, silicic acid may be separated from the solution in which it is contained, by first rendering the latter strongly acid, if it is not already so, and then evaporating the liquid to dryness. Hydrochloric acid is generally employed to acidify the solution of silicic acid. During evaporation, the silicic acid is deposited, most frequently in the form of an insoluble jelly, but occasionally in a pulverulent state: it is not, however, completely separated until the liquid is brought to perfect dryness, and the residue treated with a dilute acid to remove all soluble matters. Silicic acid then remains undissolved, generally in a state of purity, and may be collected on a filter, washed, dried, and ignited in a platinum crucible. As thus obtained, silicic acid is highly hygrometric; hence the crucible in which it is contained should be kept well covered while being cooled and weighed.

ANALYSIS OF NATURAL SILICATES.

The first ingredient of silicates whose weight should be determined in the analysis of these bodies is *water*, to estimate which a known weight of the silicate, previously deprived of all its hygrometric moisture by gentle drying (page 299.), is heated to redness in a weighed platinum crucible for about half an hour. The loss of weight sustained by the ignition indicates the amount of water contained in the silicate. For the subsequent operations it is better to employ another portion of the mineral, as silicates which have un-

dergone ignition do not dissolve so readily as before being heated.

For the purpose of analysis, silicates may be conveniently divided into two classes; those decomposable by acids, and those undecomposable by acids.

I. SILICATES DECOMPOSABLE BY HYDROCHLORIC ACID.

| | | |
|--------------|------------|---------------------------|
| Allophane | Gadolinite | Nosian |
| Analcime | Gehlenite | Okenite |
| Anorthite | Haüyne | Orthite |
| Apophyllite | Helvine | Pectolite |
| Botryolite | Heulandite | Potash-harmotome |
| Calamine | Ilvaite | Pyrosmalite |
| Cerine | Laumonite | Scapolite |
| Cerite | Lazulite | Scolezite |
| Chabasie | Leucite | Siliceous oxide of copper |
| Cronstedtite | Meerschaum | Sodalite |
| Datholite | Mesole | Stilbite |
| Diopase | Mesolite | Titanite (Sphene) |
| Epistilbite | Natrolite | Wollastonite |
| Eudialite | Nepheline | |

II. SILICATES NOT DECOMPOSABLE BY HYDROCHLORIC ACID.

| | | |
|----------------------|-------------|----------------|
| Acmite | Emerald | Petalite |
| Albite | Epidote | Pinite |
| Andalusite | Euclase | Prehnite |
| Autophyllite | Felspar | Pyroxene |
| Axinite | Garnet | Serpentine |
| Barytes-harmotome | Hornblende | Soapstone |
| Carbonated manganese | Idocrase | Soda-spodumene |
| Carpholite | Labradorite | Spodumene |
| Chlorite | Lepidolite | Staurolite |
| Chondrodite | Mica | Talc |
| Diallage | Obsidian | Topaz |
| Dichroite | Olivine | Tourmaline |

Except, however, in estimating the amount of alkali contained in the mineral, the course to be pursued in the analysis of a silicate of one class, differs from that of a silicate of the other class only at the commencement of the process.

(1.) The following is the method commonly practised in the analysis of a silicate decomposable by hydrochloric acid.

The mineral being reduced to a very fine powder, is dried at a gentle heat in a platinum crucible, to expel hygrometric moisture, weighed, and digested in hydrochloric acid in a porcelain bason. The bases formerly united to silicic acid, thereby become chlorides, and silica, having the appearance of a jelly, is set free. If the decomposition is complete, no gritty particles of the mineral are perceived on drawing the point of a glass rod across the bottom and sides of the porcelain bason.

The solution thus obtained is evaporated to perfect dryness, the residue moistened with hydrochloric acid, and then digested in hot water. The chlorides dissolve, leaving a residue of pure silicic acid, which may be filtered, washed, ignited, and weighed.

(2.) Silicates not decomposable by hydrochloric acid must be calcined with an alkaline carbonate*, a caustic alkali, carbonate of barytes, or quick-lime, and afterwards dissolved in an acid. As this operation has already been fully described when treating of the "qualitative analysis of silicates" (pages 217. 220.), any further notice of it is unnecessary.

After separation of the silica by evaporating the acid solution to complete dryness, digesting the residue in dilute hydrochloric acid, and filtering, the remaining steps in the analysis of silicates of both classes differ according to the nature of the constituents. Supposing the mineral to contain all the bases which ordinarily enter into the composition of silicates (page 217.), the usual course is, first, to add a slight excess of ammonia to the solution filtered from the silicic acid, on which *alumina* and *peroxide of iron*, with traces of oxide of manganese and magnesia, are precipitated, methods of separating which have already been described. (pages 339. and 336.) From the liquid filtered from those oxides, *lime* is precipitated by oxalate of ammonia (page 315.), and the oxalate of lime being separated, *manganese* is then thrown

* A mixture of carbonate of soda and carbonate of potash, in the proportion of single equivalents, is said to fuse at a lower temperature than either carbonate separately. Such a mixture may be obtained by calcining Rochelle salt (tartrate of potash and soda), lixiviating the calcined mass in water, and evaporating the solution to dryness.

down as sulphuret by hydrosulphate of ammonia (page 331.); *magnesia* may be precipitated afterwards by phosphate of soda and ammonia. For details of the methods of estimating and separating these bases, I must refer to what has been previously said on the subject, under each particular base.

When *magnesia* and manganese occur together, a better method than the above may be adopted, as an example of which, the following analysis of the mineral *colophonite* is subjoined. (Liebig, *Handwörterbuch*, p. 343.)

The constituents of that mineral are — silica, alumina, *magnesia*, lime, peroxide of iron, and protoxide of manganese. After fusion with an alkaline carbonate, and separation of silica in the ordinary method, the solution is mixed, first, with chloride of soda, and then with bicarbonate of potash.

The solution contains *lime* and *magnesia*.

The precipitate contains alumina, peroxide of iron, and peroxide of manganese. Treat it with solution of potash to dissolve out alumina. Dissolve the residue, which consists of peroxide of manganese and peroxide of iron, in hydrochloric acid, and saturate the solution with carbonate of barytes in the cold.

The solution contains manganese and barytes: precipitate *manganese* by hydrosulphate of ammonia.

The precipitate is peroxide of iron mixed with carbonate of barytes. Dissolve it in hydrochloric acid, and precipitate *peroxide of iron* by ammonia.

Estimation of alkalis in silicates. — The amount of alkali contained in silicates decomposable by acids, and not containing *magnesia*, may be easily determined in the following manner: — The mineral is dissolved in hydrochloric acid, and silica is separated in the usual manner. To the solution, which contains the chlorides of the bases formerly united to silica, carbonate of ammonia and some caustic ammonia are added, the solution is evaporated to dryness, the residue digested in water, and the liquid filtered from the precipitate. In the absence of *magnesia*, all the earthy bases are thereby

precipitated, and the filtered solution, when evaporated to dryness and the residue calcined, yields the alkali in the state of chloride, fit to be weighed.

But it is obvious that when fusion with an alkali is necessary to procure solution, and the ordinary method is followed, the estimation of alkali will be extremely difficult, if not altogether impracticable. Other means of effecting decomposition are then adopted in the determination of the alkali, for which another portion of the mineral must be employed, all the other constituents having been previously estimated by the usual process. Several modes are proposed of procuring the decomposition of silicates by means of substances, the presence of which would offer no impediment to the estimation of the alkali; as by means of hydrofluoric acid, by fusion with carbonate of barytes or caustic barytes, and by oxide of lead, each of which may be removed from the solution of the ignited mass in an acid, without interfering with the estimation of the alkali.

A method which gives a very satisfactory result, consists in heating to whiteness in a platinum crucible, for an hour, an intimate mixture of one part of the silicate with about six parts of finely powdered quick-lime. The silicic acid before in combination with alkali then unites with lime, and the alkali is therefore set free. The mass, which coheres considerably from the heating, is removed from the crucible after the ignition, and carefully powdered in a glazed mortar, placed on a sheet of paper to preserve any particles which may be projected. The powder is then transferred to a bason, and digested in water for ten or twelve hours at a moderate heat: the solution thus obtained is filtered, and the undissolved lime washed. The filtered liquid is merely a solution of the alkali in lime-water, from which the former may be obtained by adding a little carbonate of ammonia to the solution, boiling the mixture for some time, and filtering, to separate the carbonate of lime. The filtered solution is slightly acidified by hydrochloric acid, evaporated to dryness, and the residue of alkaline chloride is moderately calcined and weighed. Instead of performing the

latter part of the operation as indicated, the calcined mass may be treated with hydrochloric acid, by which both earths and the alkali are dissolved, and the earths precipitated by an excess of carbonate of ammonia; nothing then remains in solution but the alkali which is to be estimated and ammoniacal salts. The solution is evaporated to dryness, the residue is calcined, and the alkali weighed as chloride. The large quantity of ammoniacal salts present renders it difficult to effect the calcination of the residue without some loss of the alkali by projection.

The silica obtained in the analysis of silicates should always be tested as to purity after being weighed. This is best done by fusing a small quantity in a bead of carbonate of soda on a piece of charcoal before the blowpipe. If a colourless and transparent glass is obtained, the silica is pure, or nearly so; but if an opaque bead is produced, the silica is not free from foreign earthy matter.

SECTION II.

SULPHUR.

Estimation of sulphuric acid.—Few bodies can be determined with greater accuracy than sulphuric acid. The solution of the substance in water is acidified by nitric or hydrochloric acid, and the sulphuric acid precipitated in the form of sulphate of barytes, by adding nitrate of barytes or chloride of barium to the solution. Before filtration, the mixture should be heated to cause the aggregation of the precipitate, otherwise the latter generally passes through the pores of the filter. The precipitate must be ignited before being weighed. From the weight of the precipitated sulphate of barytes, that of the sulphuric acid it contains is calculated. If the substance to be analyzed is insoluble in

water, but soluble in dilute acids, pure hydrochloric acid should be used as the solvent. If the solvent is nitric acid, the liquid should be diluted with water, in order to prevent the precipitation of nitrate of barytes. The latter salt, though soluble in water, is insoluble in strong nitric acid; and if a little chloride of barium is added to strong nitric acid mixed with a small quantity of sulphuric acid, nitrate of barytes is precipitated in preference to sulphate of barytes.

The sulphates insoluble, or nearly so, in water and dilute acids are, sulphates of barytes, lead, lime, and strontian.

Sulphate of lead may be analyzed by fusing it with about three times its weight of carbonate of soda in a platinum crucible, by which sulphate of soda and oxide of lead are produced. All contact with organic matter must be carefully avoided, to prevent reduction of oxide of lead to the metallic state, which would inevitably destroy the crucible, by the formation of a fusible alloy of platinum with the reduced lead. When the fused mass is treated with water, the greater portion of it dissolves, leaving a residue of oxide of lead, which may be collected on a filter, and if pure, washed, dried, ignited, and weighed. If the oxide of lead is mixed with other oxides, these are separated by processes before described. To the filtered liquid, which contains sulphate and carbonate of soda, add a slight excess of hydrochloric acid, and estimate the sulphuric acid by precipitation as sulphate of barytes. The aqueous solution of the fused mass generally contains a little lead, which may be precipitated as sulphuret by sulphuretted hydrogen, and weighed as the sulphate. (page 360.)

Sulphate of barytes and sulphate of strontian are analyzed by mixing them in a minute state of division with three times their weight of a mixture of carbonate of soda and carbonate of potash, and fusing the mixture in a platinum crucible. Sulphates of soda and potash and carbonates of the earths are formed, the latter remaining undissolved when the fused mass is treated with water. When washed, the earthy carbonates are dissolved in dilute hydrochloric acid, and estimated in the usual manner. (pages 314. and 315.) The solution

filtered from the earthy carbonates is acidified by hydrochloric acid, and sulphuric acid is precipitated as sulphate of barytes by chloride of barium.

Sulphate of lime may be completely decomposed by boiling it with a solution of carbonate of potash or soda, with the formation of carbonate of lime and an alkaline sulphate. The carbonate of lime is collected on a filter, dried, and weighed after a gentle calcination, and the sulphuric acid in the filtered solution is precipitated as sulphate of barytes, the excess of alkaline carbonate being previously neutralized by hydrochloric acid. After the carbonate of lime is weighed, it should be tested for any undecomposed sulphate of lime, by dissolving it in pure dilute hydrochloric or nitric acid. If an insoluble residue remains, or if chloride of barium produces a precipitate of sulphate of barytes in the acid solution, the carbonate of lime has not been free from sulphate of lime.

From the insolubility of sulphate of barytes both in water and dilute acids, sulphuric acid in solution may be separated from almost every other substance; all the salts of barytes which are insoluble in water being soluble in hot hydrochloric acid, with the single exception of the sulphate.

Sulphurous acid, existing in a state of solution, may be estimated by converting it into sulphuric acid by means of strong nitric acid, by aqua regia, or by chlorine gas, with the application of a gentle heat; the sulphuric acid formed being afterwards weighed sulphate as of barytes.

ANALYSIS OF SULPHURETS.

The ordinary method of analyzing a metallic sulphuret consists in digesting the substance in nitric acid or aqua regia; the metal thereby oxidates, and commonly dissolves, and the sulphur is converted into sulphuric acid, which may be precipitated and weighed as sulphate of barytes. In general, the metal is oxidated and dissolved long before the sulphur; and as a continuance of the digestion is tedious, from the slowness of the action, if the undissolved sulphur

has a pure yellow colour, and does not appear to be mixed with any undecomposed sulphuret, it may be collected on a weighed filter (having first diluted the solution), washed carefully, dried, and weighed on the filter. From the filtered liquid, sulphuric acid is precipitated by chloride of barium. If the sulphuret is in a highly divided state, and the acid employed highly concentrated, the whole sulphur is sometimes immediately converted into sulphuric acid.

The metals existing in the solution filtered from the sulphate of barytes are then separated and estimated in various ways by processes already treated of. If the presence of barytes, arising from the excess of chloride of barium employed, interferes with the determination of these metals, the barytes may first be removed by adding sulphuric acid to the solution. It is in general, however, more convenient to operate upon another quantity of the material for the determination of the bases. Weak nitric acid should not be employed to dissolve some metallic sulphurets, as an evolution of sulphuretted hydrogen gas might then be occasioned, with a consequent loss of sulphur.

In all cases in which sulphur is separated in the elementary state, especially in the analysis of metallic sulphurets, the purity of the sulphur should be tested, after being weighed, by volatilizing it in a weighed porcelain crucible. If any fixed residue remains in the analysis of a metallic sulphuret, it is commonly the oxide of the metal, and was of course weighed in the state of sulphuret with the sulphur. After a strong calcination of the residue in the open air, to ensure perfect oxidation, and also to expel any sulphuric acid which may have been formed, it is weighed; and the nature of the oxide being known, the weight of *sulphuret* which it represents is calculated and deducted from the weight obtained of sulphur. When this oxide is dissolved in hydrochloric acid, there usually remains a trace of stony matter or silicic acid undissolved, if the substance analyzed is a natural sulphuret.

In this manner, most metallic sulphurets may be analyzed; but a small number require slight modifications of the above

process. *Sulphuret of silver* must be decomposed by pure nitric acid, and not by aqua regia: when the decomposition of the sulphuret is complete, and the liberated sulphur is separated from the solution, silver may be precipitated by hydrochloric acid; and after filtration from the chloride of silver, sulphuric acid may be precipitated by chloride of barium. *Sulphuret of bismuth* must also be treated with nitric acid, and not with aqua regia. The liberated sulphur being collected and washed with dilute nitric acid, bismuth is precipitated from the solution by carbonate of ammonia, and sulphuric acid from the filtered liquid by chloride of barium.

Native sulphuret of lead (common lead ore, or galena,) may be analyzed by digesting it in fuming nitric acid, by which it is converted into the insoluble sulphate of lead. The excess of acid being expelled by evaporation to dryness, the residue is digested in a solution of caustic potash until the sulphate of lead is completely dissolved. The alkaline solution is filtered from the earthy matters which remain undissolved, and treated with sulphuretted hydrogen, until all the lead in solution is precipitated as sulphuret, which is converted into sulphate of lead, and estimated in the usual way. (page 360.) As the *sulphurets of mercury* cannot be decomposed by nitric acid, it is necessary to use aqua regia to dissolve these compounds. The sulphuric acid produced is precipitated by chloride of barium, and mercury is thrown down from the filtered liquid by sulphuretted hydrogen. (page 375.)

The combinations of sulphur with most metals may be analyzed by heating the substance in an atmosphere of chlorine gas. In this operation, the apparatus *fig. 21.* (page 351.) may be employed. Chloride of sulphur and chlorides of the metals are thereby formed: the former, together with the volatile metallic chlorides, distills into the receiver, which should be kept one-fourth filled with water; the fixed chlorides remain in the bulb. Before applying heat to the sulphuret in the bulb, all the air in the receiver should be displaced by chlorine. The chloride of sulphur which distills is decomposed, on coming in contact with the water in the receiver,

with formation of free sulphur and hydrochloric and sulphurous acids; the latter is immediately converted into sulphuric acid by chlorine in the presence of water. The sulphur is collected in a weighed filter, and solution of chloride of barium is added to the filtered liquid to precipitate sulphuric acid. The metallic chlorides remaining in the bulb may be dissolved out by water, and estimated by the ordinary processes.

The following mode of analyzing metallic sulphurets, particularly sulphuret of copper, has been recently recommended by Dr. Kemp. The sulphuret, in fine powder, is mixed with about three times its weight of dry chlorate of potash, and the mixture is placed in a test-tube of hard Bohemian glass. The mortar in which the mixture is made is rinsed out with a little fresh chlorate, which is also introduced into the tube. The mixture is then heated rather sharply, heat being first applied to the top, and then downwards to the bottom. The oxidation of the sulphuret is complete in less than a minute. When cold, the contents of the tube are washed out into a flask with hydrochloric acid, the mixture is digested at a moderate heat for a few minutes, then diluted, filtered from the undissolved silica, and the sulphur (sulphuric acid) and metals in the solution estimated in the usual way.

The analysis of *alkaline* and *soluble earthy sulphurets* may be performed in the following manner:—A solution of chloride of copper is added to the aqueous solution of the substance to be analyzed, and the precipitate, which is sulphuret of copper, is rapidly collected on a filter, and oxidized by fuming nitric acid. When the sulphur is completely dissolved, a solution of nitrate of barytes is added to precipitate the sulphuric acid into which the sulphur has been converted, and the amount of sulphur is calculated from that of the sulphate of barytes obtained. If the alkaline sulphuret is treated at once with nitric acid, some sulphur would escape oxidation and be lost, being evolved in the state of sulphuretted hydrogen gas; hence the necessity of having the sulphur in the state of sulphuret of copper, which does not yield sulphuretted hydrogen with strong nitric acid. The

liquid, filtered from the precipitated sulphuret of copper may be treated with sulphuretted hydrogen, to separate copper; and the alkali or earth remaining in solution may be determined in the usual manner.

Instead of mixing the solution of chloride of copper with the solution of the alkaline or earthy sulphuret, sulphuretted hydrogen gas may be produced by decomposing the sulphuret by hydrochloric acid, and the gas transmitted through solutions of the copper salt, contained in a series of Woulf's bottles, the last solution being supersaturated with ammonia. When the decomposition is complete, a saturated solution of carbonate of ammonia should be introduced into the generating bottle, to cause a stream of carbonic acid gas to traverse the whole apparatus, and thus carry forward the remaining sulphuretted hydrogen. The precipitated sulphuret of copper is treated by nitric acid as above.

Estimation of the sulphur in cast iron.—The small quantity of sulphur contained in cast-iron may be estimated by dissolving the iron in dilute sulphuric acid, and conducting the evolved gases through a metallic solution capable of absorbing the sulphuretted hydrogen, for which purpose the ammonio-nitrate of silver has been recommended. A bulbed apparatus, similar to that employed for absorbing ammonia in the estimation of nitrogen*, but containing four bulbs of equal size between the two large bulbs, will be found convenient for containing the solution of silver in this operation. (Dr. Bromeis.)

SECTION III.

CHLORINE.

Analysis of chlorides.—Hydrochloric acid and chlorine may be determined with great accuracy. The solution of

* See the figure of this apparatus under the head of "Determination of Nitrogen," in the chapter on Organic Analysis.

the substance to be analyzed is warmed, and the chlorine is precipitated in the form of chloride of silver by adding a solution of nitrate of silver to the liquid. Chloride of silver falls much better from a neutral liquid (provided the nitrate of silver is applied in slight excess) than from a liquid containing a free acid. In many cases, however, the presence of a free acid is necessary in order to prevent the precipitation of other compounds of silver besides the chloride, such compounds being mostly soluble in free acids. Certain precautions to be observed in the precipitation and ignition of chloride of silver have already been mentioned under the subject of silver. (page 369.) From the liquid filtered from the chloride, the excess of silver may be removed by adding hydrochloric acid or common salt, and the bases present may then be determined by the ordinary processes. If the substance is insoluble in water, but soluble in acids, such as many subchlorides, nitrid acid should be employed as the solvent.

Chloride of silver and *chloride of lead* may be analyzed by reducing these compounds to the metallic state by hydrogen gas, in the apparatus *fig. 20.* (page 345.), with the assistance of heat; hydrochloric acid gas is then disengaged. The degree of heat required for the decomposition of metallic *chlorides* by hydrogen gas is somewhat higher than that necessary to decompose the *oxides* of the same metals by hydrogen. When the decomposition of the chloride is complete, which is known by the absence of white fumes on holding a rod moistened with ammonia at the extremity of the apparatus, the tube *c* containing the reduced metals may be disconnected from the apparatus and weighed. The weight of the tube and substance having been previously determined, the loss of weight on reduction represents the amount of chlorine contained in the chloride.

Subchloride of mercury (calomel) may be analyzed by digestion in a solution of caustic potash; the black suboxide of mercury and chloride of potassium are then formed. The filtered alkaline solution is saturated with nitric acid, and the chlorine contained in it is precipitated by nitrate of silver.

It is advantageous to take another portion of calomel to determine the mercury by means of protochloride of tin.

Separation of chlorine from hydrochloric acid. — This may be effected by means of metallic mercury. When a mixture of free chlorine and free hydrochloric acid, in aqueous solution, is agitated with excess of metallic mercury, the whole of the free chlorine is absorbed by the mercury, with formation of subchloride of mercury (calomel), which is insoluble in water. The free hydrochloric acid remains in solution, unaffected by the mercury, and may be estimated in the usual way. Chlorine water is conveniently tested for free hydrochloric acid in this way.

CHLORIMETRY.

Chlorimetry, or the process for the valuation of chloride of lime (bleaching powder), is an important subject in connection with the chemical arts. This article of commerce is subject to considerable deterioration through exposure to air; and its actual value as a bleaching agent can only be determined by making an estimation of its proportion of available chlorine. Three modes of obtaining this will be pointed out, in one of which the available chlorine is determined by finding what quantity of the chloride of lime to be analyzed is required to convert a known weight of the protoxide of iron into peroxide.

For conversion into peroxide of iron, one equivalent of protoxide of iron requires half an equivalent of oxygen, which is supplied in the present process by the decomposition of half an equivalent of water by chlorine of the chloride of lime. Half an equivalent of chlorine, therefore, or 17.72 parts, effects this change upon a whole equivalent, or 35.18 parts of protoxide of iron, which quantity of protoxide is contained in one equivalent, or in 138.5 parts of crystallized protosulphate of iron. Therefore 17.74 parts of chlorine can peroxidize 138.5 parts of crystallized protosulphate of iron, or 10 grains of chlorine can peroxidize 78.1 grains of the crystallized protosulphate. Now the process consists in dis-

covering how much of the specimen of chloride of lime is requisite to peroxidize 78.1 grains of the protosulphate, which quantity of the chloride must contain 10 grains of chlorine.

In the first place, 78.1 grains of the pure protosulphate (clean crystals of the salt dried by strong pressure between folds of cloth) are dissolved in about two ounces of water, and the solution is acidulated by a few drops of hydrochloric or sulphuric acid. Fifty grains of the chloride of lime are weighed out, mixed well in a mortar with about two ounces of tepid water, and the mixture poured into an alkalimeter. (page 306.) The measure is filled up to 0 with the washings of the mortar, and the liquids are well mixed by agitation, the mouth of the alkalimeter being closed by the palm of the hand. This solution of chloride of lime is then gradually added to the solution of 78 grains of protosulphate of iron until the latter is completely peroxidized, which is discovered by means of the red prussiate of potash. That salt gives a precipitate of prussian blue with a salt of the protoxide of iron only, and not with a salt of the peroxide; so long, then, as it produces a blue precipitate, protoxide of iron still exists in solution, and more chloride of lime must be added. In applying red prussiate as the test, it is convenient to have a white plate spotted over with small drops of its solution very dilute, which are touched with the drop of the liquid to be tested, taken out on the point of a glass stirrer. Stopping short exactly at that point at which the red prussiate of potash ceases to afford prussian blue, but gives a green colour, the number of measures poured from the alkalimeter is carefully observed: the richer in chlorine the specimen of chloride of lime is, the less of course is required. As this amount, whatever it may be, but which, for example, we will suppose to be 70 measures, contains always 10 grains of chlorine, it becomes a simple matter to calculate the per-centage of chlorine in the specimen. For as 100 of the alkalimeter divisions contain 50 grains of the chloride, each single measure must contain half a grain; the 70 measures poured out contained, therefore, 35 grains of chloride of lime. Then, if 35 grains

of the chloride contain 10 grains of chlorine, by simple proportion, 100 grains of the chloride must contain 28·57 grains of chlorine. The only calculation to obtain the per-centage is, to divide 1000 by one half the number of measures poured from the alkalimeter: —

$$\frac{1000}{35} = 28\cdot57.$$

Or, what is the same thing, to divide 2000 by the actual number of measures poured out.*

The other two chlorometrical processes to be noticed are similar in principle to the preceding, but the material employed to absorb the chlorine, in the place of copperas, is arsenious acid in one case, and the yellow prussiate of potash in the other.

When arsenious acid is exposed to free chlorine in the presence of water, it becomes converted into arsenic acid; the latter, however, is without action on free chlorine. One equivalent of arsenious acid (99·37), and two equivalents of free chlorine (70·94), in the presence of two equivalents of water, give rise to one equivalent of arsenic acid and two equivalents of hydrochloric acid: 10 parts of chlorine are therefore absorbed by 14·0 parts of arsenious acid. A solution is made of 14 grains of pure arsenious acid in about an ounce and a half of diluted muriatic acid, and the solution is tinged slightly blue by the addition of a drop or two of solution of sulphate of indigo. (page 36.) Fifty grains of the bleaching powder to be tested are well mixed with warm water in a mortar, and the mixture and washings of the mortar poured into the ordinary alkalimeter up to the mark O, the mixture being well shaken. This liquid is then poured, by very small portions at a time, into the arsenical solution, with constant agitation, until the slight blue tinge of the latter is wholly destroyed, which is an indication that the bleaching liquid has been applied in excess. After the com-

* In the preceding process, Mr. W. Crum uses a stoppered phial to contain the solution of sulphate of iron, which is shaken, instead of an open jar or tumbler, and thus prevents any escape of chlorine. He can then add the chloride of lime in a dry state, from a weighed quantity, in the absence of an alkalimeter. (*Trans. Glasgow Phil. Society.*) -

plete conversion of the arsenious acid into arsenic acid, two or three drops of the bleaching liquid suffice to destroy the blue colour of the indigo. As each measure of the alkalimeter represents half a grain of chloride of lime, and the number of measures poured out contain 10 grains of chlorine, therefore the per-centage of chlorine is obtained by dividing 2000 by the number of measures required for bleaching the indigo.

To avoid the trouble of weighing out 14 grains of arsenious acid for every experiment, it is convenient to have a stock solution of that acid of a certain strength, from which a measure containing exactly 14 grains may be poured out. Such a solution may be made by dissolving 280 grains of pure arsenious acid in 8 or 10 ounces of hydrochloric acid free from arsenic, and diluting the solution with water until the liquid measures exactly 30 ounces. One ounce and a half of such a solution is the quantity to be used for each test, as that measure contains 14 grains of arsenious acid.

The chlorometrical process in which yellow prussiate of potash* is used to absorb the chlorine, is conducted in just the same manner, with the substitution of 119·7 grains of the crystallized prussiate for the 14 grains of arsenious acid. By the action of one equivalent of free chlorine, two equivalents of the yellow prussiate are converted into one equivalent of the red prussiate, with formation likewise of one equivalent of chloride of potassium. As soon as the whole of the yellow prussiate is converted into the red prussiate, the mixture ceases to afford prussian blue with a solution of peroxide of iron; but, until that point is attained, the solution of 50 grains of chloride of lime is poured from the alkalimeter, by very small portions at a time, with constant agitation. The solution of peroxide of iron may be made by adding a little nitric acid and muriatic acid to a hot solution of copperas, until the liquid loses the dark colour it first acquires, and becomes reddish yellow: the liquid may then be evaporated nearly to dryness, and the residue diluted with a large quantity of water. The solution, which should be very dilute, is

* The use of the yellow prussiate of potash in Chlorimetry was first pointed out to me by my friend Mr. J. Mercer, of Oakenshaw.

applied in drops to a white plate, and the drops are touched by the point of a glass rod with the liquid to be tested.

The number 2000, when divided by the number of measures of solution of chloride of lime necessary to prevent the prussiate from striking a blue colour with the drops of solution of peroxide of iron, gives the per-centage of chlorine in the sample required.*

* The following observations by Mr. Crum describe a method of testing weak solutions of chloride of lime, such as are used in bleaching, which appears to be well adapted to the use of the practical bleacher. The original paper is published in the Proceedings of the Glasgow Philosophical Society. "Chlorimetry requires to be practised by the bleacher for two purposes—First, he has to learn the commercial value of the bleaching powder which he purchases; and with that view he can scarcely desire any thing better than the method either by arsenious acid, or green copperas. But the more important, because the hourly testing of his bleaching liquor, and that on which the safety of his goods depends, is the ascertaining the strength of the weak solutions in which the goods have to be immersed. If the solution is too strong, the fabric is apt to be injured. If too weak, parts of the goods remain brown, and the operation must be repeated. The range within which cotton is safe in this process is not very wide. A solution standing 1° on Twaddell's hydrometer (spec. grav. 1.005) is not more than safe for such goods, while that of half a degree is scarcely sufficient for the first operation of stout cloth, unless it is packed more loosely than usual. When the vessel is first set with fresh solution of bleaching powder, there is little difficulty, if the character of the powder be known; but when the goods are retired from the steeping vessels, they leave a portion of bleaching liquor behind, unexhausted, which must be taken into account in restoring the liquor to the requisite strength for the next parcel. The chlorimeter must, therefore, be applied every time that fresh goods are put into the liquid.

"I introduced another into our establishment some years ago, which has been in regular use ever since, and by which the testing is performed in an instant. It depends on the depth of colour of the peracetate of iron. A solution is formed of protochloride of iron, by dissolving cast-iron turnings in muriatic acid, of half the usual strength. To ensure perfect saturation, a large excess of iron is kept for some time in contact with the solution at the heat of boiling water. One measure of this solution, at 40° Twaddell, (spec. grav. 1.200) is mixed with one of acetic acid, such as is sold at 8s. a gallon. That forms the proof solution. If mixed with six or eight parts of water it is quite colourless, but chloride of lime occasions with it the production of peracetate of iron, which has a peculiarly intense red colour.

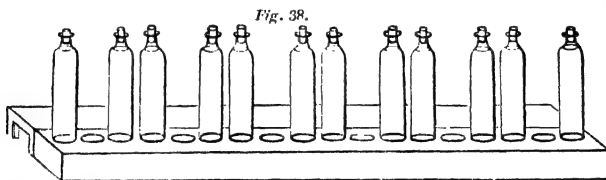
"A set of phials is procured, 12 in number, all of the same diameter. A quantity of the proof solution, equal to $\frac{1}{3}$ th of their capacity, is put into each, and then they are filled up with bleaching liquor of various strengths, the first at $\frac{1}{12}$ th of a degree of Twaddell, the second, $\frac{2}{12}$ ths, the third, $\frac{3}{12}$ ths, and so on up to $\frac{12}{12}$ ths, or 1 degree. They are then well corked up, and ranged together, two and two, in a piece of wood, in holes drilled to suit them. We have thus a series of phials, showing the shades of colour which those various solutions are capable of producing. To ascertain the strength of an unknown and partially exhausted bleaching liquor, the proof solution of iron is put into a phial similar to those in the instrument, up to a certain mark, $\frac{1}{3}$ th of the whole. The phial is then filled up with the unknown bleaching liquor, shaken, and placed beside that one in the instrument which most resembles it. The number of that phial is its strength in 12ths of a degree of the hydrometer; and, by inspecting the annexed table, we find at once how much of a solution of bleaching powder, which

SECTION IV.

IODINE.

Analysis of iodides.—The amount of iodine contained in iodides which are soluble in water may be estimated by pre-

is always kept in stock, at a uniform strength of six degrees, is necessary to raise the whole of the liquor in the steeping vessel to the desired strength.



“The instrument is formed of long 2-ounce phials cast in a mould; those of blown glass not being of uniform diameter. The outside, which alone is rough, is polished by grinding, and in this state they can easily be procured at 4s. 6d. a dozen. They are placed two and two, so that the bottle containing the liquid to be examined may be set by the side of any one in the series, and the colour compared by looking through the liquid upon a broad piece of white paper stretched upon a board behind the instrument.

“To explain the table it is necessary to state that the steeping vessels we employ contain, at the proper height for receiving goods, 1440 gallons, or 288 measures of 5 gallons each,—a measure being the quantity easily carried at a time. In the following table, 0 represents water, and the numbers 1, 2, 3, &c. are the strength of the liquor already in the vessel in 12ths of a degree of Twaddell, as ascertained by the chlorimeter. If the vessel has to be set anew, we see by the first table that 32 measures of liquor at 6° must be added to (256 measures of) water to produce 288 measures of liquor at $\frac{5}{12}$ ths of a degree. But if the liquor already in the vessel is found by the chlorimeter to produce a colour equal to the second phial, then 24 measures only are necessary, and so on.”

| To stand $\frac{8}{12}$ ° | | | | To stand $\frac{6}{12}$ ° | | | |
|---------------------------|---|----|---|---------------------------|---|----|---|
| 0 requires 32 measures. | | | | 0 requires 24 measures. | | | |
| 1 | — | 28 | — | 1 | — | 20 | — |
| 2 | — | 24 | — | 2 | — | 16 | — |
| 3 | — | 20 | — | 3 | — | 12 | — |
| 4 | — | 16 | — | 4 | — | 8 | — |
| 5 | — | 12 | — | 5 | — | 4 | — |
| 6 | — | 8 | — | | | | |
| 7 | — | 4 | — | | | | |

| To stand $\frac{4}{12}$ ° | | | | To stand $\frac{3}{12}$ ° | | | |
|---------------------------|---|----|---|---------------------------|---|---|---|
| 0 requires 16 measures. | | | | 0 requires 12 measures. | | | |
| 1 | — | 12 | — | 1 | — | 8 | — |
| 2 | — | 8 | — | 2 | — | 4 | — |
| 3 | — | 4 | — | | | | |

precipitating the iodine in the form of iodide of silver by the nitrate of silver. The precipitated iodide is collected and ignited in the same manner and with the same precautions as the chloride of silver. This method of estimating iodine is of course not applicable when either chlorine or bromine is also present.

The proportion of iodine existing in a neutral liquid may be directly estimated by means of a solution composed of 1 part of crystallized sulphate of copper, and $2\frac{1}{2}$ parts of crystallized protosulphate of iron. On adding such a solution, all the iodine is precipitated in the form of subiodide of copper; the chloride of copper which might be formed at the same time from the chlorides that might be present remains in solution. The precipitate must be collected on a weighed filter, washed, dried, and weighed. It contains 66.6 per cent. of iodine. The amount of iodine contained in iodine ley may be conveniently determined by this process. A solution of sulphate of copper in a saturated aqueous solution of sulphurous acid may be made use of in this operation in the place of the solution of the sulphates of copper and iron.

Protochloride of palladium is another reagent employed for the direct determination of iodine. The mixture of the protochloride of palladium with the iodide is allowed to stand for ten or twelve hours, or until the brownish black precipitate of protiodide of palladium has subsided, and the supernatant liquid become clear. The precipitate is then collected on a filter, washed, dried at 212° , and then weighed: 179.9 parts of the protiodide contain 126.57 of iodine.

It is, however, usual to determine the amount of iodine as *loss*, that is, as the deficiency on the weight of the original substance, having ascertained the quantity of all the other ingredients of which the substance is composed. To obtain, then, the amount of base combined with iodine, the iodide may be decomposed by sulphuric acid in a porcelain capsule with the assistance of heat; hydriodic acid, sulphurous acid, and iodine are evolved, and a residue remains, consisting of the sulphate of the oxide of the metal formerly united to iodine. The composition of the iodide being known, the

weight of metal in the portion weighed is calculated and deducted from the original weight of the substance, to obtain the amount of iodine. In the case of iodides, whose metallic bases are precipitated from solution in an acid by sulphuretted hydrogen or hydrosulphate of ammonia, those reagents may be used to separate the metals. If the iodide for analysis is insoluble both in water and acids, it should be ignited with carbonate of soda, and the heated mass afterwards digested in water. Iodide of sodium and the excess of carbonate of soda dissolve, and leave the metallic oxide as a residue, if it is insoluble in a solution of the alkaline carbonate. The oxide may be weighed, the corresponding amount of metal calculated, and deducted from the original weight of the iodide to obtain the amount of iodine.

Separation of iodine from chlorine. — As iodides rarely exist in nature unmixed with chlorides, it is important to have the means of completely separating chlorine from iodine. Many processes have been proposed for this purpose, one of the best of which is the following, by M. Rose: — Both chlorine and iodine are precipitated from the mixed salts by nitrate of silver, and the mixed iodide and chloride of silver is collected, ignited, and weighed. The mixed iodide and chloride is then introduced into a tube of hard glass, having a bulb blown on its middle (such as the tube *c* of the apparatus figured at page 345.), and after being weighed with the tube, chlorine gas is passed over the substance. By the action of chlorine, the iodide of silver is decomposed, chloride of silver being formed, and iodine liberated, which may be driven out of the tube by the application of heat. On again weighing the tube, a loss will be experienced, which, multiplied by 1·389, gives the quantity of iodine contained in the mixed chloride and iodide of silver operated on. The number 1·389 bears the same proportion to 1 which the equivalent of iodine bears to the difference between the equivalents of chlorine and iodine. For every equivalent of iodine (126·57) expelled by chlorine one equivalent of chlorine (35·47) is absorbed; the loss actually sustained in the experiment, therefore, is the difference between the equivalents of chlo-

rine and iodine, or 91.1 for every 126.57 parts of iodine, which numbers are as to 1 to 1.389. Having thus obtained the iodine, the amount of chlorine may be calculated by deducting the weight of the iodide of silver (found by calculation) from the weight of the mixed chloride and iodide of silver; the remaining chloride of silver contains 24.67 per cent. of chlorine.

SECTION V.

BROMINE.

The amount of bromine contained in bromides may be estimated either by precipitation, as bromide of silver, which is collected and fused with the same precautions as the chloride of silver, or by determining the amounts of all the other ingredients, and estimating bromine as the loss on the original weight of the substance. The amount of metallic base may be ascertained either by conversion into sulphate by heating the bromide with sulphuric acid in a porcelain capsule, or by separating the metal from the solution of the substance by means of sulphuretted hydrogen or hydrosulphate of ammonia. Bromides insoluble in acids may be analyzed by fusion with carbonate of soda, in a manner precisely similar to that described for insoluble iodides.

Separation of bromine from iodine.—In a mixed bromide and iodide the respective proportions of bromine and iodine may be ascertained by a method similar to that proposed by M. Rose for the analysis of mixed chlorides and iodides. The mixture of iodide and bromide of silver is obtained, its weight determined, and the mixture is heated in an atmosphere of bromine. A loss is found to occur after the heating, which, multiplied by 2.627, gives the proportion of iodine.

Separation of bromine, iodine, and chlorine.—A mixture of a bromide, an iodide, and a chloride, in neutral aqueous solution, may be analysed in the following manner:—The solution is divided into two equal parts; one is mixed with

excess of nitrate of silver and the precipitate, which consists of a mixture of chloride, iodide and bromide of silver, is collected, washed, dried, and weighed. The iodine in the other half of the solution is estimated as protiodide of palladium (see page 419.); the liquid filtered from the protiodide of palladium is treated with sulphuretted hydrogen in order to remove the excess of palladium as insoluble sulphuret, which is separated by filtration. The filtered liquid is boiled to dissipate the excess of sulphuretted hydrogen, and then mixed with an ammoniacal solution of chloride of silver, prepared by mixing a saturated solution of chloride of silver in ammonia with one measure of ammonia and one of water. Such a solution precipitates bromine as bromide of silver, but produces no precipitate in a saturated solution of chloride of sodium (Schweitzer). The weight of the bromide of silver, together with the quantity of iodide of silver equivalent to that obtained of protiodide of palladium, is deducted from the weight of the mixed chloride, iodide, and bromide of silver: the remainder is, of course, the weight of the chloride of silver, from which that of the chlorine required is calculated.

SECTION VI.

FLUORINE.

Analysis of fluorides. — The ordinary method of determining the amount of fluorine contained in fluorides consists in separating the fluorine in the state of hydrofluoric acid, and calculating its quantity from the loss. To perform this, the dry weighed fluoride is moistened with oil of vitriol in a platinum capsule, and heated so long as acid vapours are given off. The residue, which consists of the sulphate of the oxide of the metal formerly in combination with fluorine, is weighed, and the proportion of *metal* it contains calculated; the weight of the metal deducted from the original weight of the substance leaves the amount of fluorine. If more than one base is combined with fluorine in the substance for

analysis, it is necessary to undertake a full determination of the bases, and to calculate the amount of each *metal*. To obtain the amount of fluorine, the united weight of the metals is deducted from the weight of the fluorides operated on.

When the substance to be analyzed contains water, that, it is obvious, will be included in the loss, and must therefore be estimated by another operation before the fluorine can be determined. The amount of water contained in many fluorides may be estimated by heating the substance alone to redness in a platinum crucible. The whole of the water may then be given off in a pure state, and its amount is learned by the loss in weight undergone by the heating. But it frequently happens, that besides the water a little hydrofluoric acid is disengaged, which vitiates the determination of the former. In such a case, the weighed fluoride, in fine powder, is intimately mixed with freshly calcined and powdered protoxide of lead, the mixture is introduced into a small hard glass retort, and covered with a little more pure oxide of lead. The retort, with its contents, is weighed, and heated to redness to expel water, which is given off without a trace of acid, the latter being retained by the oxide of lead. The vapour of water in the retort at the close of the operation is removed by carefully sucking it out with the mouth by means of a narrow tube introduced into the retort through the neck. The loss in the weight of the retort indicates the amount of water expelled. By deducting the water from the united loss of fluorine and water previously arrived at by the determination of the bases, the amount of fluorine is ascertained.

SECTION VII.

PHOSPHORUS.

Estimation of phosphoric acid.—In the analysis of combinations of phosphoric acid with substances, the weights of

which are easily determined, it is usual, having obtained the amount of every other ingredient, to consider the deficiency on the weight of the matter employed as representing the phosphoric acid.

If contained in a neutral or ammoniacal solution, phosphoric acid is best precipitated as the double phosphate of magnesia and ammonia, by adding a solution of a salt of magnesia and some free ammonia to the solution containing a phosphate. For the precautions necessary to be observed in the precipitation of that double salt, see page 318. By the calcination to which it is subjected previous to being weighed it parts with all its ammonia, becoming converted into phosphate of magnesia containing 63.33 per cent. of phosphoric acid.

If phosphoric acid exists alone in solution, its amount may be determined directly, by adding, of pure and freshly calcined protoxide of lead, a known weight, which is in excess, to the solution, and evaporating to dryness. The residue, which is a mixture of phosphate of lead with the excess employed of oxide of lead, is calcined in a platinum crucible, and weighed. The increase on the quantity of protoxide of lead employed is the amount of phosphoric acid formerly contained in solution.

Phosphoric acid is also sometimes estimated directly by precipitation from its *neutral* solutions as phosphate of lead or as phosphate of barytes; but as this acid forms compounds of different composition with the same base, the precipitate must, in general, be subjected to analysis after its weight is determined, in order to ascertain the actual amount of phosphoric acid it contains. The phosphate is analyzed by ascertaining directly the proportion of base it contains, and considering the loss as the phosphoric acid.

The two phosphates mentioned are analyzed by the following processes:— *Phosphate of lead* is dissolved in dilute nitric acid, and oxide of lead is precipitated from the solution as sulphate, by sulphuric acid; some alcohol is added to the mixture to prevent the solution of any trace of the sulphate, the latter being wholly insoluble in dilute alcohol. The precipitated sulphate of lead is filtered, washed with weak alco-

hol, ignited, and weighed. From the quantity of sulphate, that of oxide of lead is calculated, and the phosphoric acid estimated as loss. *Phosphate of barytes* is analyzed by dissolving it in hydrochloric acid, and precipitating barytes from the solution by sulphuric acid. From the weight of the precipitated sulphate of barytes, that of the barytes is calculated, which, again, deducted from the original weight of the phosphate, gives the amount required of phosphoric acid.

Phosphoric acid may be separated from many metallic oxides by fusion with an excess of carbonate of soda. The mass, after being heated, contains the metallic oxide, phosphate of soda, and the excess of carbonate of soda. If the oxide is quite insoluble in a solution of the alkaline carbonate, nothing but phosphate of soda and carbonate of soda dissolves when the dry mass is treated with water. The aqueous solution is first saturated with hydrochloric acid, then rendered slightly ammoniacal, and mixed with a salt of magnesia, to precipitate the phosphoric acid as phosphate of magnesia and ammonia.

Separation of phosphoric acid from alumina.—Phosphoric acid cannot be separated from alumina by the above method, as phosphate of alumina is soluble in solution of carbonate of soda. To analyze phosphate of alumina, Fuchs recommends that a known weight of the combination should be dissolved in a solution of caustic potash, and the alumina be precipitated by a solution of silicate of potash, in the form of silicate of alumina and potash. The bulky and mucilaginous precipitate which falls is collected on a filter, washed, and digested in hydrochloric acid; the acid mixture is evaporated to dryness to separate silica. When the dry mass which remains after the evaporation is moistened with hydrochloric acid, and then treated with water, it affords an insoluble residue of silicic acid, while alumina dissolves, and may be precipitated from the solution by carbonate of ammonia. The alkaline liquid filtered from the precipitate of silicate of alumina contains all the phosphoric acid. It is supersaturated with hydrochloric acid and evaporated to dryness; the residue is redissolved in water, the solution rendered alkaline

with ammonia, and the phosphoric acid precipitated as phosphate of magnesia and ammonia. (page 424.)

Phosphate of alumina may also be decomposed by calcination with a mixture of carbonate of soda and silica. When the calcined mass is digested in water, phosphate of soda, with the excess of carbonate of soda, and some silicate of soda dissolves, while silicate of alumina remains undissolved.

Separation of phosphoric acid from peroxide of uranium.—Phosphate of uranium in a finely divided state, such as that of a precipitate from a solution by ammonia, is completely soluble, according to M. Ebelmen, in a solution of bicarbonate of potash. (See page 60.) From such a solution, peroxide of uranium may be precipitated by caustic potash, in the form of uranate of potash, while the phosphoric acid remains in the alkaline solution. Or else the phosphoric acid may be first separated from the solution by the addition of a known quantity of peroxide of iron dissolved in nitric acid, the bicarbonate being in excess; a precipitate falls consisting of the whole of the peroxide of iron and phosphoric acid, the increase in weight of which represents the amount of phosphoric acid required. The peroxide of uranium may afterwards be estimated in the usual manner. (M. Ebelmen.)

Another, but less accurate, method consists in dissolving the phosphate in hydrochloric acid, supersaturating the solution with ammonia and applying hydrosulphate of ammonia, in order to convert all the oxide of uranium into sulphuret, which is collected, washed, dissolved in hydrochloric acid, and estimated as usual. The phosphoric acid in the ammoniacal liquid filtered from the sulphuret of uranium is precipitated as phosphate of magnesia and ammonia. (page 424.)

Separation of phosphoric acid from sulphuric acid.—If a substance is to be analyzed which contains both phosphoric and sulphuric acids, the latter may be easily separated from the former by the solubility of phosphate of barytes in acids. Either hydrochloric or nitric acid being first mixed with the solution, on adding an excess of chloride of barium, sulphate of barytes only is precipitated, which may be weighed. If the solution filtered from the precipitate of sulphate of barytes

is carefully neutralized with ammonia, phosphate of barytes is precipitated, the phosphoric acid contained in which may be determined by weighing and analyzing the precipitate, in the manner before described.

M. Schulze has proposed a method of determining the amount of phosphoric acid contained in soils, rocks, wood-ashes, &c., founded on the insolubility of phosphate of the peroxide of iron, and phosphate of alumina in acetic acid. In soils, the phosphoric acid generally exists in the state of phosphate of lime and phosphate of magnesia. If to a solution of these phosphates in acetic acid a sufficient quantity of a solution of acetate of peroxide of iron is added, all the phosphoric acid may be precipitated, in the form of phosphate of the peroxide of iron, which may be collected and weighed. Instead of acetate of iron, acetate of alumina may be employed with a similar result. As soils usually contain more peroxide of iron and alumina than is sufficient to combine with the whole of the phosphoric acid they contain, all that is required to be done, is estimating the amount of this acid contained in a soil, is to add excess of ammonia to the solution of the earthy matter in hydrochloric acid, and to treat the precipitate with acetic acid. Nothing but phosphate of the peroxide of iron and phosphate of alumina remains undissolved, and after being weighed, these phosphates may be separated from each other by dissolving the latter in solution of caustic potash.*

An important modification of the preceding process, applicable, however, only in the absence of alumina, has been introduced by M. Liebig. The acid solution of the earthy phosphate is mixed first with a solution of perchloride of iron, and afterwards with excess of ammonia. Instead of digesting the mixture thus precipitated of phosphate of peroxide of iron and peroxide of iron in acetic acid, it is digested in hydrosulphate of ammonia, whereby sulphuret of iron and phosphate of ammonia are produced. After a little digestion,

* The insolubility of the phosphate of the peroxide of iron in acetic acid also affords a means of separating the peroxide from the protoxide of iron; the phosphate of the latter base being soluble in acetic acid.

the sulphuret of iron is collected on a filter and washed, and the phosphoric acid is precipitated from the filtered liquid as phosphate of magnesia and ammonia. (page 424.)

SECTION VIII.

BORON.

Estimation of boracic acid. — Boracic acid is best determined by the loss experienced on the original weight of the substance containing it, when the weight of every other constituent is ascertained. The estimation of boracic acid comes thus to consist in the perfect separation and determination of the weights of all the substances with which it is associated. The separation of the metals proper from boracic acid may be easily effected by sulphuretted hydrogen or hydrosulphate of ammonia, but the separation of the earths requires particular processes. When the compounds which contain this acid are decomposable by concentrated sulphuric acid, they may be analyzed by the following method, proposed by Arfvedson. A known weight of the borate to be analyzed is mixed in a platinum crucible with four times its weight of pure fluor spar, both substances being in a state of fine powder, and sufficient oil of vitriol to make a thick paste. The mixture is heated gradually to redness, and maintained at that temperature so long as any acid vapours are given off. All the boracic acid is thus converted into the gaseous fluoride of boron, which is entirely disengaged, together with the excess of sulphuric acid. The residue consists of sulphate of lime produced from the decomposition of fluor spar, and sulphates of the bases with which boracic acid was previously in combination. This residue is then subjected to a full analysis, by processes described elsewhere; and the nature and proportions of the bases being ascertained, their unite weights are deducted from the original weight of the borate operated on to obtain the amount of boracic acid.

In the manner just described may be analyzed all borates

which are decomposable by sulphuric acid, and which do not contain water. The same process may be followed if the borate contains lime; the quantity of fluor spar must then be accurately weighed, and the lime contained in the substance analyzed be deduced from the excess of sulphate of lime formed over the calculated quantity produced from the quantity of fluor spar employed. (Rose.)

Instead of fluor spar, hydrofluoric acid may be used to decompose borates. The borate, in a state of fine division, is mixed with hydrofluoric and sulphuric acids in a weighed platinum crucible: the mixture evaporated to dryness and calcined to expel all the excess of sulphuric acid, leaves a residue, consisting of sulphates of the bases formerly united with boracic acid.

Borate of barytes may be analyzed by dissolving it in hydrochloric or nitric acid, and precipitating barytes from the solution, as sulphate, by sulphuric acid. The weight of the barytes contained in the sulphate being calculated, the boracic acid may be estimated as loss.

C. G. Gmelin has proposed the following process for the direct determination of boracic acid. The powdered substance to be analyzed is heated to redness with carbonate of soda, and the resulting mass is digested in water, to dissolve the borate formed during the fusion. The small quantities of silica and alumina which the water may also dissolve are precipitated by digestion with carbonate of ammonia. The filtered liquid is evaporated to dryness, and the residue treated with sulphuric acid, to decompose the borate of soda; the boracic acid thus liberated is dissolved out by alcohol. The alcoholic solution, when saturated with ammonia, evaporated to dryness, and the residue calcined, leaves pure boracic acid, whose weight may be determined.

SECTION IX.

NITROGEN.

Estimation of nitric acid. — If nitric acid exists in solution in a free state, and unmixed with any other acid (except sulphuric), its amount may be determined by adding a sufficient quantity of barytes water to render the liquid feebly alkaline, and evaporating the solution of nitrate of barytes thus obtained to dryness. The excess of barytes combines with carbonic acid from the atmosphere during evaporation, to form the insoluble carbonate of barytes, which therefore remains undissolved when the dry residue is treated with water. The barytes in solution is then precipitated by sulphuric acid, and weighed as sulphate. The weight of the sulphate of barytes is, of course, proportional to that of the nitric acid, in the ratio of single equivalents of each.

When the nitric acid exists in a state of combination, it is generally estimated as loss, the amount of the base in combination with the acid being ascertained, either by conversion into sulphate, or by other means proper for the particular base.

If the base is one which may be precipitated from its acid solutions by sulphuretted hydrogen, that re-agent is advantageously employed to separate it from nitric acid. The precipitated sulphuret being separated from the solution, the nitric acid set at liberty may be determined by adding a slight excess of barytes water to the solution, and evaporating to dryness. The small quantity of sulphuret of barium formed from the sulphuretted hydrogen in solution is converted, during evaporation, into hyposulphite and sulphate of barytes, both insoluble salts. When the dry mass is treated with water, nothing but nitrate of barytes dissolves, which may then be converted into sulphate, and the latter weighed. When the analysis is performed in this manner, it is necessary to cease passing sulphuretted hydrogen so soon as the nitrate is entirely decomposed, as an excess of the re-agent would act on the liberated nitric acid, occasioning its decomposition and consequent loss.

Such *subnitrates* as are insoluble in water may be decomposed, as well as if soluble, by sulphuretted hydrogen; they should be reduced to a state of minute division, and diffused through an ounce and a half or two ounces of water. These ~~bodies~~ may likewise be decomposed by digestion in a solution of sulphuret of barium; by which an insoluble metallic sulphuret is produced, on the one hand, and the soluble nitrate of barytes on the other. The excess of sulphuret of barium is removed from the solution by a current of carbonic acid gas, which precipitates carbonate of barytes, and causes an evolution of sulphuretted hydrogen gas. The solution is filtered and evaporated to dryness, the residue redissolved in water, and barytes precipitated from the solution by sulphuric acid. From the amount of sulphate of barytes, that of the nitric acid may be calculated.

The nitric acid in nitrates may also be estimated directly by distilling the nitrate with sulphuric acid and treating the product of distillation as described in the first paragraph of the present section. Barytes water may be introduced into the receiver at first. If the nitrate under examination is mixed with an iodide, a bromide, or a chloride, some sulphate of silver should first be added to the solution of the mixture in a neutral state in order to convert the iodide, bromide, or chloride into a sulphate; after removal, by filtration, of the precipitated iodide, bromide, or chloride of silver, the liquid is mixed with a slight excess of carbonate of soda, concentrated by evaporation, if necessary, mixed with more than enough pure sulphuric acid to convert all the bases present into bisulphates, and then distilled into a receiver containing barytes water. The distillation is carried on until fumes of sulphuric acid begin to make their appearance. The barytes solution in the receiver is treated as described above.

Processes for the "Refraction of Nitre" are noticed in the Appendix.

EUDIOMETRY.

To separate *oxygen* gas from *nitrogen* gas, and to determine the amounts of *watery vapour* and *carbonic acid* contained in

atmospheric air, several processes have been recommended, possessing various claims to accuracy as well as simplicity. Of those for estimating the oxygen and nitrogen the principal are the following:—

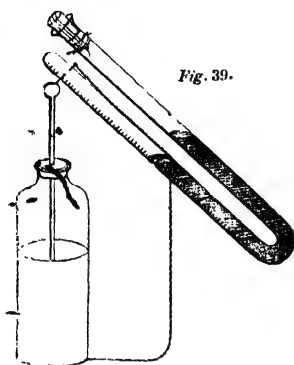
(1.) Into a measure of air observed at a known temperature and pressure, and contained in a narrow graduated tube standing over water, a stick of phosphorus is introduced and allowed to remain for twenty-four hours, or so long as any absorption of gas is seen to occur. When the white vapours have entirely disappeared, the phosphorus is withdrawn, and the amount of contraction noticed, together with the temperature and pressure, for which, if they do not agree with the observations at the time of the first measurement, corrections must be made*: the gas remaining is nitrogen. This is the simplest method, but probably the least exact.

(2.) Gay-Lussac recommends a method in which oxygen is separated from nitrogen by means of slips of copper moistened with hydrochloric acid, which absorb oxygen with rapidity.

(3.) Another simple method is that in which the oxygen is estimated by observing the contraction which occurs on the ignition of a mixture of a known measure of air with one half its bulk of pure hydrogen. The ignition may be effected either by the electric spark or by means of a pellet of clay and spongy platinum. In the latter case, combination of the hydrogen and oxygen takes place without explosion; hence the experiment may be performed in a common graduated tube standing over mercury. One third of the contraction represents the volume of oxygen contained in the measure of air employed. In igniting by the electric spark, Dr. Ure's eudiometer is a convenient instrument to be used. It is formed of a straight glass tube (*fig.* 39.), about twenty inches in length, sealed at one end, and doubly bent at the middle. The limb with the sealed end is graduated. Two platinum wires are sealed into the glass near the closed end, with their extremities within the tube about one tenth of an inch

* The means of making these corrections are given in an Appendix.

apart. On placing one of these wires in communication with



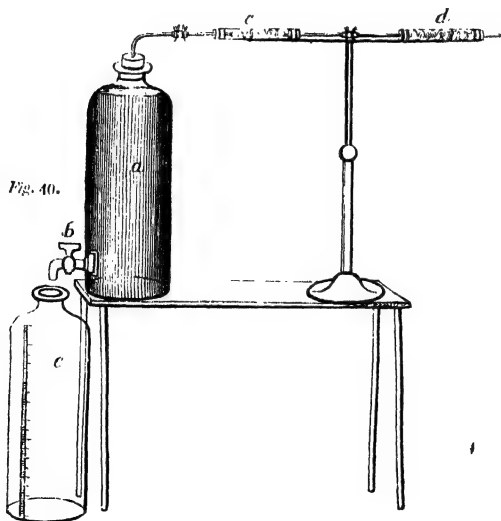
the knob of a charged Leyden jar, and the other with the outside, the spark passes within the tube. Having prepared a mixture of air and hydrogen in known proportions, enough of this mixture is transferred into the tube at the water or mercurial trough, to occupy about three inches of the sealed limb; the amount of the mixture introduced is accurately observed, the liquid standing in both limbs at the same level.

The mouth of the open limb is now closed by a cork which is secured by a wire, and the electric spark is taken through it. After the explosion, a contraction is found to occur, to observe the amount of which, the liquid must again be brought to the same height in both limbs. One third of the contraction is the bulk of oxygen contained in the original mixture.

(4.) The most accurate mode of determining the composition of the air is that lately employed by M. Dumas, which is a modification of a process previously proposed by M. Brunner. After the air is passed through potash and sulphuric acid successively, to absorb carbonic acid, water, and carburetted hydrogen, it is conducted over metallic copper heated to redness in a tube of hard Bohemian glass. The copper employed is that procured from reduction of the oxide by means of hydrogen gas. Oxygen is eagerly absorbed by the copper, while nitrogen passes onwards, and is received into a weighed exhausted globe, which is again weighed at the close of the experiment. The increase in the weight of the tube containing the copper gives at once the oxygen. In this process, therefore, both the oxygen and nitrogen are determined by direct weighing, and no corrections are required for changes of temperature and pressure: hence its superiority to all eudiometrical processes in which the gases are estimated by measurement.

The proportion of *carbonic acid gas* contained in the atmosphere may be determined by adding gradually barytes-water or lime-water of a known strength to the air to be examined, contained in a large globe of known capacity. The liquid is dropped into the globe by means of a graduated pipette, so long as the alkaline reaction of the barytes or lime is neutralized, which is best ascertained by reddened litmus paper. When the paper is rendered permanently blue, more barytes or lime has been added than is necessary to form carbonate with all the carbonic acid of the air. The carbonic acid is proportional to the quantity of lime or barytes neutralized. —

The most ready method of determining the amount of *watery vapour* in the air is by the hygrometer; but the subject of hygrometry belongs rather to physics than to chemistry. The same object may be attained by causing a known quantity of air to pass through a tube which contains some highly hygroscopic body; a method followed by Brunner. A cylindrical bottle, *a* (*fig. 40.*), furnished with a stop-cock *b*, near



its bottom, is connected (air-tight) at top with a small tube *c*, containing fragments of dry chloride of calcium; and that is connected, by means of a caoutchouc joint, with the tube

d, which contains asbestos moistened with concentrated sulphuric acid, an extremely useful hygrometric agent. The tube *d* being weighed, and the apparatus mounted as in the figure, the stopcock is opened, and the water which flows out is received in the graduated vessel *e*. That vessel serves as the measure of the air which enters the bottle *a*. If passed with a moderate degree of rapidity, the air, in entering, is entirely deprived of its water by the sulphuric acid in the tube *d*; the increase in weight of which at the end of the experiment is the amount of water contained in a volume of air equal to the volume of water collected in the receiver *e*.

SECTION X.

CARBON.

Analysis of carbonates.—The quantity of carbonic acid contained in all carbonates which are soluble in hydrochloric or sulphuric acid in the cold may be determined by the following simple method:—A known weight of the powdered substance is introduced into a flask similar to that represented in *fig. 41*. The flask should be thin at the bottom to allow of

Fig. 41.



the application of heat, and have the capacity of three or four ounces of water. It is fitted with a cork, which has a perforation to admit a small bent tube, and the latter is connected by means of another cork with a somewhat larger tube, *a*, containing fragments of dry chloride of calcium. The extremity *b* of this tube is drawn out so as to be capillary. The small tube *c* within the flask, sealed at one end, is intended to

hold hydrochloric or sulphuric acid to decompose the carbonate, and is of such length that it will not fall flat on the bottom of the flask, but rest against the side at an angle of about 45° with the bottom, so that on inclining the flask, all

the acid contained in this tube can be made to flow out. The apparatus being ready, the weighed carbonate is introduced into the empty flask, with about half an ounce of water; the small tube *c*, containing sufficient hydrochloric or sulphuric acid to decompose the carbonate, is then introduced, taking care that no acid comes in contact with the carbonate, and the flask is closed by the cork attached to the chloride of calcium tube *a*. The whole apparatus is now weighed, after which the flask is inclined, in order that a little of the acid in the tube *c* may flow out and come in contact with the carbonate, which is repeated until the latter is completely decomposed. As the evolved carbonic acid gas is dried in its passage through the chloride of calcium tube *a*, nothing else than this gas escapes, and the loss in weight of the apparatus at the close of the experiment is the weight of the carbonic acid required. But as the flask is then full of carbonic acid gas, which is considerably heavier than air, it should not be weighed in its present state. To get rid of the remaining carbonic acid, the flask is gently heated, so as to fill it with aqueous vapour, and thus drive out the gas, the steam itself not proceeding further than the chloride of calcium tube. On the condensation of the steam, air enters the flask, which, when cold, is in the same condition as to weight as it was when weighed before the decomposition of the carbonate, save only in the loss of carbonic acid.

The carbonic acid gas remaining in the flask at the close of the decomposition may be more easily removed by affixing to the cork of the flask another small tube open at both ends; one end may reach nearly to the bottom of the flask, and the other an inch or so from the cork, so as to be conveniently closed by the finger during the decomposition, in order to prevent the passage of the gas through that tube. At the close of the decomposition the flask is very gently heated, merely to expel the carbonic acid dissolved in the acid solution; another chloride of calcium tube is then attached by a cork to the end of the open tube; and the carbonic acid having been first blown out through the tube *a*, by the mouth applied to the other chloride of calcium tube, fresh air is sucked in by

applying the mouth to a perforated cork or small tube adapted to *b*. The flask is then in a fit state to be weighed.

In the analysis of alkaline carbonates by this method, it is better to employ dilute sulphuric than hydrochloric acid, as a little hydrochloric acid gas might easily be carried away by the carbonic acid, or evaporated on heating the flask at the close of the operation; but for earthy carbonates whose sulphates are insoluble, the employment of sulphuric acid is not admissible. Lime-stones and marls are analyzed very conveniently by this process.

Carbonates of oxides of the metals proper, which do not contain water, or any other volatile constituent, excepting carbonic acid, may be analyzed by simply heating a known weight of the substance to redness in a weighed platinum crucible. The loss in weight experienced by heating is the amount of carbonic acid.

(For the methods of estimating carbonic acid when contained in aqueous solution see "Analysis of Mineral Waters.")

ANALYSIS OF GUNPOWDER.

Separation of carbon from sulphur and nitrate of potash. — The process of analyzing gunpowder consists, first, in the separation of nitrate of potash from carbon and sulphur, and, second, in the separation of carbon from sulphur. The gunpowder, when reduced to a fine powder and weighed, is boiled in about seven times its weight of water, to dissolve the nitre. The residue, which consists of carbon and sulphur, is collected on a weighed filter, washed with tepid water so long as any nitrate of potash is dissolved out, dried and weighed. The filtered solution of nitrate of potash is evaporated to dryness in a weighed platinum capsule in a water-bath, and the dry saline residue weighed. This residue generally contains a small quantity of chloride of sodium, to determine the quantity of which, the dry salt, after being weighed, is dissolved in water, and the amount of chlorine it contains is estimated by precipitating and weighing as the chloride of silver. The amount of chloride of sodium which

corresponds to the weight of the chloride of silver is calculated, and deducted from the weight of the nitrate of potash previously obtained.

Various methods are practised to ascertain the relative proportions of carbon and sulphur. One consists in converting all the sulphur into sulphuric acid, which is weighed as sulphate of barytes. For this purpose, 1 part of the dry mixture of carbon and sulphur is mixed, first with 4 parts of carbonate of potash (free from sulphate), and afterwards with 8 parts of nitre, and 6 parts of chloride of sodium. When that mixture is heated strongly in a platinum crucible, the sulphur becomes sulphuric acid, which unites with potash. After being heated, the mass is dissolved in water, and the excess of alkaline carbonate is neutralized with hydrochloric acid: sulphuric acid is then precipitated in the form of sulphate of barytes, which is washed, dried, and weighed. The quantity of sulphur which corresponds to the weight of the sulphate of barytes is calculated, and the carbon is estimated as loss.

Another method of separating the sulphur and carbon, advantageous from its allowing the weights of both these elements to be taken directly, consists in dissolving out the sulphur from the mixture by means of sulphite of potash; hyposulphite of potash is thus formed, and a residue of pure carbon remains, which is collected on a weighed filter, dried, and weighed. From the solution of hyposulphite of potash all the sulphur may be precipitated by the addition of hydrochloric acid: the precipitate is collected on a weighed filter, washed, dried, and weighed. (Pelouze.)

Two other methods are also practised; in the first of these carbon and sulphur are separated from each other by subliming the latter in an atmosphere of hydrogen, and weighing the residue of carbon; in the second, by heating the mixture in an atmosphere of chlorine, when the volatile chloride of sulphur is formed. But neither of these methods possesses any advantage over those described, while their execution is more difficult.

Separation of carbon from iron: analysis of cast-iron. —

The estimation of carbon contained in cast-iron may be effected by an operation similar to that of an organic analysis. (Regnault.) From 70 to 80 grains of the specimen is reduced to powder (either by pulverizing in a mortar or by filing), and mixed with from 12 to 14 times its weight of chromate of lead, previously fused and reduced to powder. About one third or one fourth of the mixture is set aside; the remainder is mixed with as much powdered chlorate of potash as the weight of cast-iron operated on, and this mixture is introduced into a tube of hard glass similar to that used in organic analysis, but much shorter. The remaining mixture of cast-iron and chromate of lead is now added, being placed above the mixture previously introduced, and the tube is connected with the potash apparatus employed in organic analysis. Heat is first applied to that part of the tube, the mixture in which contains no chlorate of potash, and is advanced gradually to the other end of the tube, the heat being increased very considerably at the close of the operation, so as to fuse the chromate of lead. By this means, the whole carbon of the cast-iron is converted into carbonic acid, which is condensed by the solution of potash. It is unnecessary to give the details of this process here, as they are all included in the account of the operation of organic analysis. A process by which the amount of sulphur in cast-iron may be determined is described at page 411.

SECTION XI.

WATER.

Estimation of water as contained in hydrates. — The ordinary method of determining the amount of water contained in a substance consists in expelling the water by the application of heat, and estimating it by the loss in weight which the substance then experiences. The degree of heat requisite varies according to the facility with which the water is expelled, and also with the nature of the hydrate under ex-

amination. Either a platinum or porcelain crucible may be employed in this operation.

In general, this simple process gives a satisfactory result, but a large number of bodies containing water exist, which can experience a change in weight on being heated, from circumstances entirely unconnected with the presence of water. For such compounds, the process must be modified. If the hydrate to be analyzed possesses the property of uniting with oxygen at a high temperature, to obtain the water, the substance is heated in an atmosphere of some gas which exerts no action on it, such as carbonic acid or hydrogen; a current of which, previously dried by being passed through a chloride of calcium tube, is sustained during the whole operation. Such an apparatus as that figured at page 345. may be used; and the water given off by the substance may be collected and weighed in a small chloride of calcium tube attached to the posterior extremity of the tube *c*. At the end of the process, and when the substance is cold, air is admitted into the tube, to bring it to the same state as when weighed before the experiment. The loss in weight indicates the amount of water.

When the substance to be analyzed contains an ammoniacal salt, that is expelled, together with the water, by ignition. The entire loss in weight being determined, the amount of ammonia contained in the substance must then be ascertained by a separate experiment; the corresponding quantity of ammoniacal salt is calculated and deducted from the whole loss, to obtain the amount of water.

In determining the proportion of water in those salts which lose the whole or a portion of their acid at a high temperature, the substance should be intimately mixed with a known weight of a strong base which can retain the acid, forming a salt which is not decomposed at the temperature at which water is given off. Protoxide of lead is the base generally employed for this purpose, of which oxide, from four to six times the weight of the substance may be taken. On applying heat, water alone is expelled, unless the compound contains an ammoniacal salt, when free ammonia is also given off.

In a case where the hydrate to be analyzed is that of an organic body, if the whole of the water is not removed by heating at a temperature lower than that at which the organic matter suffers decomposition, recourse must be had to an ultimate organic analysis, provided the substance possesses a definite constitution. The whole of the water is then obtained, condensed in the chloride of calcium tube (see the account of the operation), but with it an additional quantity proceeding from the combustion of the hydrogen of the organic substance; the proportion of which in relation to the carbon being known, the quantity of water it should produce is calculated and deducted from the whole amount obtained. The remainder is the quantity which existed in the substance as water. In the determination of combined water, care should be taken that the body is entirely free from hygrometric moisture, and if in a crystallized state, that it contains no water lodged mechanically between the plates of the crystals. If such is suspected, the crystals must be powdered and carefully dried by heating a few degrees above the ordinary temperature. The proportion of hygrometric water contained in an organic substance, such as guano, may be determined by the loss in weight which occurs on exposure to air, over oil of vitriol, as described at p. 299.

As almost all hydrates of definite constitution evolve different quantities of water at different elevations of temperature, it is advisable to commence by heating the substance gently, and to increase the temperature progressively, weighing at each increase. This is especially necessary in all accurate investigations of hydrates of salts or of organic bodies: after drying as much as possible in the open air, the substance may be kept in a confined portion of air, supported over a surface of oil of vitriol; then in vacuo, over oil of vitriol; afterwards it may be heated to 212° by a water-bath, or higher, if necessary, by means of a boiling saturated solution of some salt, such as chloride of sodium or nitre.

The proportion of water contained in inorganic hydrates which do not part with their water by being heated is estimated as the loss, the weight of all the other constituents of the substance being first determined.

ANALYSIS OF MINERAL WATERS.(1.) *Saline, Chalybeate, and Carbonated.*

Although the qualitative analysis of a mineral water may exhibit the presence of some bodies of rare occurrence, such as iodine, bromine, nitric acid, strontian, lithia, ammonia, &c., the quantities of these are, in general, so small as to render it worthless, except in special investigations, to attempt to estimate their weight. The following directions for the quantitative analysis of mineral waters will not, therefore, be complicated with details of the modes of estimating such bodies (for which I refer to other parts of this work), but comprise the means of estimating those only which are of ordinary occurrence. In saline, chalybeate, and carbonated waters, the common constituents are: — *lime, oxide of iron, magnesia, soda, manganese, silica, sulphuric acid, chlorine, and carbonic acid.*

The operations to be performed in the estimation of the fixed constituents are: —

1. Evaporation to dryness to ascertain the whole amount of saline matter.
2. Estimation of the magnesia, lime, oxide of iron, oxide of manganese, and silica, contained in the portion of the residue of evaporation which is insoluble in water.
3. Estimation of the lime, magnesia, and oxide of iron, contained in the portion of the residue of evaporation which is soluble in water.
4. Estimation of the whole amount of lime, magnesia, oxide of iron, and silica.
5. Estimation of the whole amount of sulphuric acid.
6. Estimation of the whole amount of hydrochloric acid (chlorine).
7. Estimation of the whole amount of chlorides.
8. Estimation of the whole amount of chloride of sodium.

1. To obtain the entire amount of saline matter contained in the water, a known quantity is evaporated to dryness in a porcelain bason, or what is better, in a weighed platinum

capsule. The evaporation should be conducted below 212° to prevent ebullition, and consequent loss from spirting; but when the residue is quite dry, the heat should be gradually increased to 280° or 300° Fahr. The weight of the dry residue affords a check on the subsequent determinations. It is to be observed that some of the saline matters in this residue may be in a hydrated state, although long maintained at a temperature of 300° ; as earthy chlorides, for instance, when not united with an alkaline chloride as a double salt. If very strongly heated, the hydrated earthy chlorides are decomposed with disengagement of hydrochloric acid, while the base remains in a caustic state.

During evaporation, carbonic acid gas may be disengaged, and a precipitate formed at the same time; the latter may consist of carbonate of lime, carbonate of magnesia, and oxide of iron. These bodies were at first held in solution by the carbonic acid, and are consequently precipitated when the latter is expelled. On treating the dry residue of the evaporation with water, this precipitate, together with some silica, and perhaps oxide of manganese and alumina, remains undissolved. The solution in water may also contain portions of lime, magnesia, and oxide of iron, but these portions did not originally exist in the water as carbonates.

2. The second operation consists in the estimation of the lime, magnesia, oxide of iron, oxide of manganese, and silica contained in the precipitate formed on ebullition. The dry residue of evaporation is treated with water, and as much of the precipitate as can be easily removed is thrown on a filter and washed. What remains of the precipitate attached to the sides of the capsule, after being washed, is dissolved in hydrochloric acid, and the acid liquid passed through the filter to form a solution of the whole precipitate. The filtered liquid is evaporated to dryness in order to render any silica which may be present insoluble; the residue is treated with dilute hydrochloric acid, and the solution passed through the same filter. The *silica* remaining on the filter is washed, ignited, and weighed. The analysis of the filtered acid solution is conducted according to the following table: —

TREATMENT OF THE SOLUTION IN HYDROCHLORIC ACID OF THE PRECIPITATE FORMED DURING EBULLITION.

Add a few drops of nitric acid to the solution to convert the protoxide of iron which may be present into peroxide, and apply heat. Neutralise the free acid with ammonia; add, first, muriate of ammonia, and afterwards hydrosulphate of ammonia.

The precipitate is sulphuret of iron and sulphuret of manganese: filter, wash, and dissolve it in hydrochloric acid: heat the solution to expel sulphuretted hydrogen, and saturate it, when cold, with carbonate of barytes.

To the solution, which may contain lime and magnesia, add hydrochloric acid; boil the mixture to expel sulphuretted hydrogen, and filter; add to the filtered solution first a slight excess of ammonia, and then oxalate of ammonia. Filter.

The precipitate is oxide of iron, mixed with carbonate of barytes. Filter and dissolve it in hydrochloric acid, and add excess of ammonia to the solution.

Oxalate of lime may be precipitated. It should be converted into carbonate by ignition, previous to being weighed (page 316.).

Add phosphate of soda and ammonia to the filtered solution to precipitate magnesia, if present. Convert the precipitated ammonio-phosphate of magnesia into *phosphate of magnesia* by ignition, previous to weighing it (page 318.).

Peroxide of iron is precipitated and may be dried and weighed. After being weighed, the peroxide of iron should be dissolved in muriatic acid and be tested for *alumina*.

3. The estimation of the lime, magnesia, and iron contained in the soluble portion of the residue of evaporation is performed in the manner indicated in the preceding table, pure ammonia being substituted for hydrosulphate of ammonia to precipitate oxide of iron.

4. The fourth operation is merely confirmatory of the last two, having for its object the determination of the entire amounts of lime, magnesia, iron, manganese, and silica contained in the water. A little nitric acid is added to a known volume of the water, which is evaporated carefully to dryness. On treating the residue with very dilute nitric acid, silica remains undissolved, which may be collected and weighed, and the solution is proceeded with according to the table.

5. The fifth operation is to determine the whole amount of sulphuric acid. Add a little hydrochloric acid to a known volume of the water, and estimate the sulphuric acid as sulphate of barytes.

6. To another portion of the water add an excess of nitric acid, and precipitate the chlorine by nitrate of silver. Weigh the chloride of silver, and calculate its amount of chlorine.

7. To determine the whole amount of chlorides, boil a portion of the water, and filter from the precipitate produced thereby. To the filtered liquid add muriate of ammonia, and evaporate to dryness by a water-bath, the evaporation being commenced in a porcelain bason and terminated in a weighed platinum capsule. When the saline residue is quite dry, the heat should be increased so as to bring it to a state of fusion, after which it may be weighed. The residue consists of a mixture of the chlorides with the sulphate contained in the water, the latter being either sulphate of soda or sulphate of lime. Having previously determined which of these sulphates exists by the qualitative analysis of the water, the amount of the *sulphate* is calculated from the quantity of *sulphuric acid* before obtained. On deducting the weight of the sulphate from that of the saline residue the weight of the chlorides is determined. The addition of muriate of ammonia is necessary to prevent decomposition of chloride of magnesium by ignition: the hydrated chloride gives off

hydrochloric acid, and leaves magnesia when heated to redness, but the double chloride of magnesium and ammonium, which is formed when muriate of ammonia is brought into contact with chloride of magnesium, gives off muriate of ammonia, and leaves anhydrous chloride of magnesium, which undergoes no change by being heated.

8. The amount of chloride of sodium is ascertained in the following manner:—A known weight of the water is concentrated by evaporation, and filtered from the precipitated earthy carbonates.

Barytes-water is added to the filtered solution.

The precipitate contains magnesia, lime, and sulphate of barytes. Filter.

The solution contains lime, barytes, soda, and chloride of sodium. Add to it a solution of carbonate of ammonia; boil the mixture well and filter.

The precipitate contains carbonate of barytes and carbonate of lime.

The filtered solution affords, when evaporated to dryness *and the residue calcined*, a mixture of chloride of sodium and carbonate of soda. Dissolve this residue in nitric acid, and estimate the chlorine as chloride of silver. From the weight of the chloride of silver that of the chloride of sodium is calculated.

If the analysis is exact, the chlorine contained in the chloride of sodium deducted from the whole amount of chlorine, should, in general, leave a quantity equivalent to the calcium and magnesium which remain in solution after boiling

Estimation of the volatile constituents of saline waters.—The volatile constituents of saline waters are carbonic acid, and free oxygen and nitrogen. Carbonic acid is one of the most important ingredients of some kinds of mineral waters. It may exist either in the free state, or united with lime, magnesia, oxide of iron, or soda. Several methods of determining the proportion of carbonic acid have been devised, the one most generally practised, but perhaps the least accurate

of which, consists in boiling a known quantity of the water in a flask which has an exit tube terminating under an inverted graduated bell-jar of mercury. In this jar the gases evolved by ebullition are collected. Potash being introduced into the gas, the carbonic acid is absorbed, from which absorption, the requisite corrections for pressure, temperature, and humidity being attended to, the amount of carbonic acid capable of expulsion from the water by boiling is estimated. The precipitate formed during ebullition contains a certain amount of carbonic acid, which amount may be calculated after the composition of the precipitate is ascertained by analysis, and added to that collected as gas, to obtain the entire quantity. Instead of collecting the gas over mercury, the exit tube may be made to dip into a solution composed of a mixture of chloride of calcium and ammonia, when all the carbonic acid is precipitated in the form of carbonate of lime, which may be weighed.

A simpler and more accurate method of determining the entire amount of carbonic acid in a mineral water is the following:—A known quantity of the water, which need not be very considerable, fresh from the spring, is mixed with caustic ammonia. The alkali immediately combines with the free carbonic acid to form carbonate of ammonia; at the same time, all the lime and a portion of the magnesia of the water are precipitated as carbonates, together with oxide of iron and a little silica. It rarely happens that the water contains a sufficient quantity of lime salts to unite with all the carbonic acid of the carbonate of ammonia, so that to obtain all the carbonic acid in the form of an insoluble carbonate, a solution of chloride of calcium should be added. After the liquid has been boiled to enable the precipitate to subside, it is filtered, with as little exposure to the air as possible, that no additional carbonate of lime may be formed through absorption of carbonic acid from the atmosphere. While the precipitate is yet moist, the filter is folded and passed up into an inverted graduated jar, at the mercurial trough, the jar being filled with mercury. Dilute hydrochloric acid, previously saturated with carbonic acid by dissolving a fragment of chalk in it, is then

introduced into the jar by means of a bent pipette. When the acid comes into contact with the carbonates in the filter, the latter are decomposed, with evolution of carbonic acid gas, equal in quantity to the entire amount originally contained in the water operated on. According to this method, the capacity of the mercurial jar should be nearly double the volume of the water taken for analysis; but as a single jar of sufficient capacity can rarely be procured, the same result is obtained without its use in the following manner:—The precipitated mixed carbonates are collected on a weighed filter, and when perfectly washed, are dried at 212° and weighed with the filter. The entire amount of the carbonates being thus known, small weighed portions are taken successively and decomposed by hydrochloric acid in the above manner, but in a smaller mercurial jar. The mean quantity of carbonic acid afforded by five or six such experiments is taken, and the proportion calculated for the entire amount. By this means we obtain the absolute quantity of carbonic acid contained in the water, that is, both that which exists in a free state and that which exists in the earthy carbonates. To know how much is contained in each of these states, another portion of the water is taken, equal in bulk to that before operated on, and boiled for half an hour to precipitate the carbonates, which are collected on a filter. When this precipitate is decomposed by hydrochloric acid in the mercurial jar in the manner described, it affords the quantity of carbonic acid existing in the carbonates only, which, deducted from the entire amount previously obtained, of course leaves the proportion of carbonic acid existing in the free state.

A much simpler means of determining the amount of carbonic acid in the precipitated carbonates would be by the use of the little apparatus for the analysis of carbonates described page 435.

Besides carbonic acid, all waters which are exposed to the atmosphere hold in solution free *oxygen* and *nitrogen*. To determine the proportions of these gases, the water is boiled in a flask, to the cork of which an exit tube is adapted, leading into the mercurial trough, and terminating under an in-

verted jar filled with mercury. In this jar the evolved gases are collected. The flask and tube should be completely filled with the water for examination. When all the gas is collected in the jar, introduce into it, first, a stick of potash, to absorb carbonic acid, and into the remaining air, or a portion of it; a stick of phosphorus. The latter, in a short time, absorbs all the oxygen, leaving a residue of pure nitrogen.

(2.) *Alkaline Waters.*

As bicarbonate of potash rarely enters into the composition of a mineral water, if it is ascertained that an alkaline bicarbonate does exist, the base may generally be considered to be soda. When other soluble salts are present, the accurate estimation of the alkali requires operations of some difficulty. To obtain the alkali, first, a known bulk of the water, previously well boiled, is slightly acidified by nitric acid, and its amount of chlorine determined as chloride of silver. Another portion of the boiled water, also a known quantity, is then mixed with some muriate of ammonia, and evaporated carefully to dryness, the evaporation being terminated in a platinum capsule heated by a water-bath. During the boiling, the carbonate of soda contained in the water, and the muriate of ammonia added, suffer mutual decomposition, affording carbonate of ammonia and chloride of sodium: instead of carbonate of soda, therefore, the residue of the evaporation contains the equivalent quantity of chloride of sodium. After being brought to a state of perfect dryness in the water-bath, the residue is ignited at a red heat, dissolved in water, and the amount of chlorine contained in the solution estimated as chloride of silver. Now the excess in the amount of chlorine here obtained over that before determined as pre-existing in the water is the quantity of chlorine contained in the chloride of sodium which was formed from the decomposition of the alkaline carbonate, from which, therefore, the amount of the latter can be obtained by calculation.

The carbonic acid and other ingredients of alkaline waters are determined in the same manner as in saline waters.

If both potash and soda are to be determined, one of the processes prescribed for the estimation of these alkalis (at page 303. is followed. The most convenient is that in which the alkalis are converted into neutral sulphates: the total weight of the mixed sulphates is first obtained, and afterwards the proportion of sulphuric acid.

(3.) *Sulphureous Waters.*

In a sulphureous water the most important ingredient is sulphur, which element may exist both in the state of free sulphuretted hydrogen, and as a soluble sulphuret. The proportion of sulphur may be obtained by the following process, first described by Wöhler:—To a known quantity of the water is added a solution of nitrate of silver, with which a sufficient quantity of caustic ammonia has been previously mixed to prevent the precipitation of any chloride of silver, the latter compound being soluble in ammonia. The precipitate which falls, consisting of a mixture of sulphuret of silver and earthy carbonates, is collected on a weighed filter, and washed, first with ammonia, next with dilute acetic acid to decompose the carbonates, and, lastly, with pure water. The sulphuret of silver is dried at 212° , until it no longer loses weight, and from its amount that of the sulphur it contains is calculated.

By this operation the *whole amount of sulphur* contained in the water is ascertained. To know how much exists as free sulphuretted hydrogen, and how much as a soluble sulphuret, another operation is necessary. A known quantity of the water is boiled in an open vessel until the odour of sulphuretted hydrogen is no longer perceptible. After being boiled, the liquid is filtered, and the sulphur it now contains estimated in the same manner as before. By deducting the quantity thus obtained from the entire amount, that contained as sulphuretted hydrogen, which was expelled by ebullition, is ascertained.

When free iodine is brought into contact with sulphuretted hydrogen, or a soluble sulphuret, the latter is decomposed, affording hydriodic acid, or an iodide, with precipitation of

free sulphur. On this decomposition, M. Pasquier has lately founded an elegant method of ascertaining the presence and quantity of sulphur in a mineral water, by observing what amount of free iodine is taken up, or caused to enter into a state of combination, by a known quantity of the water. The process is as follows:—An alcoholic solution of iodine, conveniently diluted and of known strength, is carefully dropped from a graduated pipette into a known weight of the water, mixed with a little starch, until the mixture commences to assume a blue tint. So long as any sulphuretted hydrogen or soluble sulphuret is present, it is decomposed by the free iodine, which passes into a state of combination, so that the peculiar effect of iodine on starch (that of rendering it blue) is not exhibited until an excess has been added. From the quantity of iodine added, that of the sulphur which it represents may be calculated.

Ingenious and elegant as this process is, it is exposed, in its present form, to a source of error of too great importance to be overlooked. If, at first, alcohol does form, strictly, a *solution* of iodine, the latter is not very slow to react on the elements of the alcohol, forming, among other products, hydriodic acid. There is, hence, a loss of free iodine, and the solution is no longer normal. If, however, instead of alcohol, a solution of chloride of potassium or chloride of sodium is employed to form the solution of iodine, the process might be made to afford results of great accuracy.

The fixed constituents of sulphureous waters are determined in the same manner as those of saline waters.

DETERMINATION OF THE DEGREE OF HARDNESS OF WATERS.

An operation of much more general application than the complete analysis of a mineral water is a simple and ready means of determining what is called the *hardness of waters*, or in other words, the quantity of earthy bases present in solution; for which, an excellent process, affording numerical results of considerable nicety, has been recently contrived by

Dr. Clark of Aberdeen. The process consists essentially in adding a *normal solution of soap* in proof spirit, from a graduated vessel, to a known quantity of the water, until a lather is produced on agitation. As the lather is formed only when the soap is in excess, and as that cannot be the case until all the earths are precipitated, the quantity of solution of soap necessary to produce the lather is exactly proportional to the quantity of earthy bases present, that is, to the hardness of the water. The following are the details of the process.

For purposes of comparison, Dr. Clark employs "standard solutions" of chloride of calcium in distilled water: these serve to prepare the solution of soap, called the "soap test," of known strength, and also to compare or refer the degree of hardness of the water under examination. To prepare these standard solutions dissolve 16 grains of pure carbonate of lime in a small quantity of hydrochloric acid, carefully avoiding loss from effervescence; evaporate the solution to dryness, redissolve the residue in water, and again evaporate. Repeat the solution and evaporation until a neutral solution is obtained. The quantity of chloride of calcium thus obtained, affords, by being dissolved in a gallon of distilled water, what is named "the standard solution of sixteen degrees of hardness," from which all the other standard solutions are prepared. A mixture of 1 measure of this solution with 15 of distilled water constitutes the standard solution of one degree of hardness: 2 measures mixed with 14 of water, and 3 measures mixed with 13 of water, form respectively, solutions of two and three degrees of hardness. In a similar manner, solutions are prepared up to sixteen degrees.

The soap preferred, in the preparation of the soap test, is that known technically in London as "Hawes' white curd." As that is not always constant in composition, it is necessary, in order to prepare a solution of known strength, to make a preliminary trial on a small scale, to ascertain approximately what quantity of soap should be dissolved in the spirit. For this purpose a small quantity of a solution is made in the

proportion of one ounce avoirdupois of soap to one gallon of proof spirit, and the actual strength of this solution is determined as follows:—"Let 100 test measures" (a single test measure employed by Dr. Clark is the $\frac{1}{7000}$ th part of the imperial gallon, that is, a measure equal to ten grains of water,) "of the standard solution of sixteen degrees of hardness be put into a phial capable of holding twice this quantity. Into the water in this phial let the prepared trial solution of soap be gradually poured from a measure graduated into test measures; let the mixture be shaken after each addition of the solution of soap, and let the operation be continued in this manner until such time as a lather will be formed of a sufficient consistence to remain for five minutes all over the surface of the water, when the phial is placed on its side. The number of test measures thus required will be either 32, or more or less than 32. If the number prove to be 32, then more solution of soap may be made in the same proportions as in the trial solution, and the solution so made will be the soap test." If the number be more or less than 32, then proportionally more or less of the soap must be employed in preparing the soap test. "But in each case the soap test, after being prepared, should be carefully verified by a trial in the manner described, so as to ascertain whether 100 test measures of the standard solution of sixteen degrees of hardness will afford a lather with exactly 32 measures of the soap test. If not, an adjustment must be made."*

The test solution thus prepared is applied in the same manner: it is gradually added to 100 test measures (1000 grains) of the water, until, on agitation, a lather of sufficient consistence is formed to remain for five minutes when the phial is placed on its side. The water is said to correspond in degree of hardness with that standard solution which requires the same number of test measures of soap solution as itself. Thus, if 32 are required, it is said to be of sixteen degrees of hardness, 32 being the number required by the standard solution of sixteen degrees. But if to form the

* Specification by Professor Clark of a new mode of rendering certain waters less impure and hard, &c., pages 4. and 5.

CHAPTER VI.

ORGANIC ANALYSIS.

MOST organic bodies contain only three elements, namely, carbon, hydrogen, and oxygen; in addition to these, a comparatively small number of organic substances possess nitrogen, while still fewer, only carbon and hydrogen, carbon and oxygen, or carbon and nitrogen. To determine the proportions of these elements is the object of organic analysis.

- (1.) *Carbon* is determined by conversion into *carbonic acid*, which is condensed in a weighed solution of caustic potash.
- (2.) *Hydrogen* is determined by conversion into *water*, which is collected and weighed in a chloride of calcium tube.
- (3.) *Nitrogen* is determined in two ways; either by collecting it in the *free state as gas*, or by converting it into *ammonia*, and forming the ammonio-chloride of platinum.
- (4.) *Oxygen* is always determined as *loss* on the original weight of the substance.

For the conversion of carbon into carbonic acid and of hydrogen into water, and to obtain nitrogen in a free state, the organic substance is subjected to a process of combustion by oxygen. It may be burned in pure oxygen gas, as in Dr. Prout's process, but in the ordinary methods, the organic substance is mixed with some solid body capable of yielding oxygen to it on the application of heat. In the processes here described, the material employed for that purpose is either pure *oxide of copper*, *oxide of copper mixed with chlorate of potash*, or pure *chromate of lead*.

Whichever of these three is used, as the hydrogen of the organic substance is, to be weighed in the form of water, ob-

viously every pains must be taken to insure the absence of all hygrometric moisture before the weight of the substance is taken, that no water but what is actually produced in the combustion may be collected and weighed. One way of drying the substance is by means of an ordinary water-bath, the substance being contained in a shallow basin placed over a deeper one containing boiling water, or a saline solution, if the temperature of 212° is insufficient. Instead of an open basin, the substance may be placed in a U-shaped tube, one extremity of which is connected with a small chloride of calcium tube, and the other with a suction bottle similar to *a* (*fig. 40.*, page 434.), by means of which air is slowly drawn through the tube, the air being previously rendered perfectly dry by passing through the tube containing chloride of calcium at the opposite extremity of the bent tube. This is a very convenient apparatus to use when it is required to determine the quantity of water lost by the substance at the temperature of the bath, in which case another chloride of calcium tube is attached, to collect the water given off, being placed between the bent tube and the suction bottle.

As the suction bottle referred to might be difficult to procure, an efficient substitute for it may be made out of an ordinary single-mouthed bottle, of sufficient dimensions, as follows:—Three perforations are made through the cork of the bottle, in one of which terminates a small tube, in connection with the U-shaped tube containing the substance to be dried. Through another perforation, a syphon tube is passed, reaching to the bottom of the bottle, the longest limb of the syphon being outside of the bottle. The use of the third opening is to renew the supply of water in the bottle without taking out the cork, and is furnished with an air-tight plug. Water being introduced into the bottle, and the syphon completely filled, the water in the bottle is withdrawn, air entering through the U-shaped tube at the same time to supply the place of the water.

To ascertain if the substance is dry, a small portion is heated in a narrow test tube to the highest temperature which the body will support without decomposition: if a

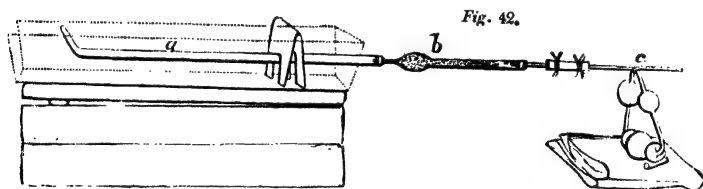
mere trace of water is present, it is discoverable by the moisture which condenses on the side of the tube.

When perfectly dry, a portion of the substance is weighed out for analysis: in general, from seven to nine grains may be taken. While being weighed, it is most conveniently contained in a glass tube sealed at one end, about two inches in length, and from one fourth to one third of an inch in diameter.

The various steps in the combustion of a pulverizable and non-volatile substance by oxide of copper are as follow:—

Preparation of the oxide of copper.—The oxide is best prepared from the nitrate by calcination in an earthenware crucible at a dull red heat until ruddy fumes are no longer evolved, and no green particles are perceived mixed with the black oxide. The nitrate itself is made by the action of nitric acid on perfectly clean pieces of sheet copper. During calcination the mass should be stirred with an iron or a copper rod.

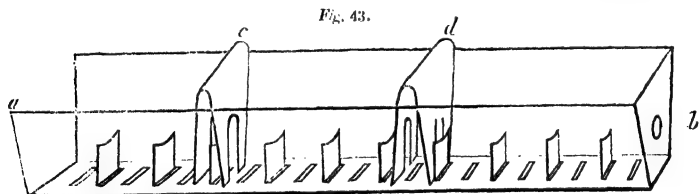
Apparatus.—The apparatus employed in the combustion is exhibited in the annexed cut: *a* is the *combustion tube*, in



which is contained the mixture of oxide of copper with the organic substance to be analyzed. The best combustion tubes are those made of hard Bohemian potash glass. In general, the tube should be about fourteen or fifteen inches long, and about four tenths of an inch in diameter: one extremity is drawn out to a point and sealed as shown in the figure, and the other is open and fused so as to receive a cork without danger of splitting. The tube should be cleaned by washing with water, and then dried perfectly by heating and sucking air out at the same time by a long narrow tube introduced to the end of the combustion tube.

By means of a perforated cork, the combustion tube is connected with the tube *b*, filled with chloride of calcium which has been strongly dried but not fused. Large fragments of that salt are placed in the bulb, and coarse powder in the tube: at each end a little cotton wool is placed to prevent any of the chloride of calcium from falling out. The use of this tube is to retain all the water produced in the combustion. Connected with the chloride of calcium tube by means of a caoutchouc joint is the potash apparatus *c*, the use of which is to absorb the carbonic acid. It consists of a tube on which five bulbs are blown, three at the bottom, the middle of which is the largest, and one on each of the sides; of the side bulbs one must be larger than the middle of the three bottom bulbs.* The extremity of this apparatus in connection with the large bulb is attached to the chloride of calcium tube. The apparatus is filled with the solution of potash by sucking with the mouth at one end, while the other end dips into a wine glass containing the liquid. It is filled in such a manner, that each of the three lower bulbs contains a small bubble of air, none of the liquid being contained in the upper bulbs. The alkaline solution is of proper strength when it possesses a specific gravity between 1.25 and 1.27.

The combustion tube is heated in a furnace (*fig. 43.*)



made of sheet iron, from 22 to 24 inches long, 3 inches high, $4\frac{1}{2}$ inches wide at top, and 3 inches wide at bottom. One end of the furnace is open *a*, the other end has a front in which is a round aperture *b* to admit the combustion tube. Across the bottom are apertures or slits, serving to form a grate; they are about half an inch distant from each other

* This, with all the other apparatus employed in organic analysis, may be procured of Messrs. R. Griffin and Co., of Glasgow.

and each aperture is one inch and a half long, and a quarter of an inch wide. At every second aperture, a support is placed for the combustion tube made of stout sheet iron.



One of these supports is represented in *fig. 44.* To confine the fire to particular portions of the tube, two screens *c* and *d* (*fig. 43.*) are employed, made of sheet iron; a figure of one of these is annexed.

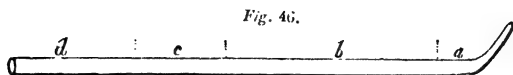
Fig. 45.



(*fig. 45.*) The furnace rests on a paving stone or a couple of flat bricks, the front projecting a little so that the first slit is open, but all the others closed. One end of the furnace is raised a little, as shown in *fig. 42.*, so that the water which condenses in the anterior part of the chloride of calcium tube may flow into the bulb.

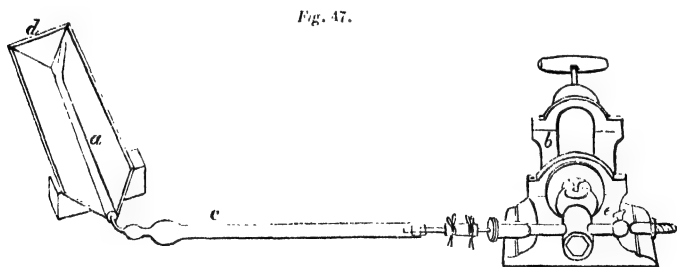
Manipulations.—The whole of the apparatus being complete, and the weights of the potash apparatus and chloride of calcium tube taken, the operator may proceed to mix the substance to be analyzed with oxide of copper. Immediately before being used, the oxide of copper is heated to dull redness in an earthen crucible, and when cooled down to about 300° or 400° , enough is introduced into the combustion tube to fill the latter a little more than one half. The object of introducing the oxide is to have a measure of the quantity necessary to mix with the substance. The mixture is best made in an unglazed Wedgwood mortar made warm by placing it on the sand bath, and rinsed out with a little clean oxide of copper from the crucible. The mortar should be placed on a sheet of highly glazed paper to retain any particles of the mixture which may be projected from the mortar. The substance to be analyzed is transferred from the tube in which it is weighed to the mortar; and the tube, with the adhering particles of the substance, is immediately placed on the pan of the balance or some place of security to be weighed at a convenient opportunity. The oxide of copper in the combustion tube is now poured gradually into the mortar, leaving about half an inch at the extremity of the tube; the oxide is mixed gently but perfectly with the substance, and the mixture is introduced into the tube. The mortar is then

rinsed out two or three times with oxide of copper from the crucible, and the rinsings are introduced into the tube, being placed above the mixture; above the rinsings is sufficient pure oxide of copper placed to reach within one inch of the open end of the tube. In *fig. 46.* *a* represents pure oxide,



b the mixture, *c* the rinsings of the mortar, and *d* pure oxide.

The tube is now closed by a cork, which (together with the perforated cork to receive the chloride of calcium tube) has been dried by heating in a bason on the sand bath for some hours, and the tube is gently tapped on a table, being held in a horizontal position, so that a clear space is seen above the oxide throughout the whole length of the tube. While the mixture is being made, both the oxide of copper and the substance absorb a quantity of water from the air, amounting to as much as 0.3 grain (equivalent to 0.5 per cent. of hydrogen), to get rid of which the mixture is dried in vacuo at a somewhat elevated temperature. The apparatus figured in the annexed cut is employed for that purpose. The combustion tube *a* is connected with an exhausting



syringe *b*, a long chloride of calcium tube *c* intervening: the combustion tube itself is placed in a wooden trough *d*, and surrounded with sand of a temperature about 250° Fahr. On exhausting the air of the apparatus by the syringe, moisture is withdrawn from the combustion tube: air, dried by passing through the chloride of calcium tube *c*, is re-

admitted by opening the stop-cock *e*, and again withdrawn. The exhaustion and admission of air having been repeated ten or a dozen times*, the combustion tube may be connected with the potash apparatus and chloride of calcium tube, arranged as in *fig. 42*. To ascertain whether all the connections are air-tight, the liquid in the potash bulbs is made

Fig. 48.



to stand higher in one side than in the other, which may be effected by sucking out a few bubbles of air from the apparatus by the suction tube *fig. 48.*, after which, the potash ley rises to supply the place of the air withdrawn. If the connections are imperfect, the liquid will return to the same level in both limbs, but not otherwise.

The apparatus being proved air-tight, the portion *d* (*fig. 46.*) of the tube which contains pure oxide of copper is now surrounded with red-hot charcoal, the heat being prevented from spreading by the screen, *fig. 45*. When that part is heated to redness, the screen is gradually advanced to the posterior end of the tube, moving from one half of an inch to one inch at a time, according to the rapidity of the evolution of gas, as perceived in the potash apparatus. As the screen is advanced, each portion of the tube must be quickly raised to a red heat, the anterior portion being all along maintained at the same temperature. During the whole combustion, particular attention must be paid to the temperature of the fore-end of the tube. It should be high enough to prevent the condensation of the smallest quantity of water within it, but not so high as to endanger the charring of the cork. The potash apparatus should not be exactly upright, but inclined a little by placing a cork under the side farthest from the tube, as shown in *fig. 42*.

At the end of the combustion, when the whole length of the tube is heated, the heat is increased by raising one side of the furnace a little to admit air through all the slits, and also by fanning from above with a piece of pasteboard. When the evolution of gas ceases or becomes very slow, the

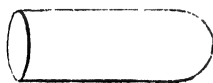
* At this period of the operation a convenient opportunity offers for weighing the tube in which the substance was weighed.

potash apparatus is restored to its horizontal position, and the ley is allowed to rise in the bulb next the chloride of calcium tube (by absorbing the carbonic acid gas), until it reaches such a height that air can enter through the three lower bulbs. The charcoal is then removed from the sealed end of the combustion tube, the point of which is divided by a small pair of pliers. Air then enters the apparatus, from the potash ley falling to the same level in both sides of the apparatus, provided there is no stoppage in the combustion tube. The suction tube (*fig. 48.*) is now adapted to the end of the potash apparatus, and a volume of air equal to about twice the capacity of the entire apparatus is slowly sucked through it. The current of air carries forward all the watery vapour and carbonic acid remaining in the apparatus, which are absorbed by the chloride of calcium and the potash. The potash apparatus and the chloride of calcium tube may now be disconnected and weighed to ascertain the increase in weight each has sustained.

Combustion of volatile organic substances by oxide of copper.

— The combustion of a volatile substance must obviously be conducted in a manner somewhat different from the preceding. If the substance is solid at common temperatures, and fusible, such as naphthaline or benzoic acid, it is fused and weighed

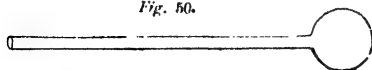
Fig. 49.



in a tube of the size and shape represented in *fig. 49.*, and both tube and substance are introduced into the combustion tube, being placed about one inch

and a half from the closed end of the latter. If the substance is liquid at common temperatures, it is weighed in one, two, or three small glass bulbs, one of which is shown of the proper

Fig. 50.



size in *fig. 50.* To fill the bulb, it is heated so as to expel a portion of the air

within, and while hot, the open end of the neck is dipped under the surface of the liquid to be introduced. When a little of the liquid has entered through the contraction of the heated air, the bulb is again gently heated, on which more air is expelled; and on dipping the open end again into the

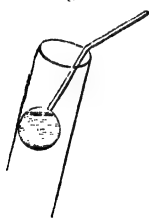
liquid, an additional quantity of the latter enters. Each bulb should be about three fourths full. The liquid being introduced, the point is sealed, and the weight of the bulb and liquid taken; the weight of the empty bulb (previously ascertained) deducted from its present weight gives that of the liquid introduced.

Fig. 51.



Before being used, the oxide of copper is heated to redness in an earthen crucible, and transferred while hot to a bulb and tube, or flask (*fig. 51.*) in which it is allowed to cool, the vessel being carefully closed with a well-dried cork. When the oxide is quite cold, the flask is uncorked, its mouth is applied to the open end of the combustion tube, and one inch or one inch and a half of oxide is shaken in. If the substance for analysis is a solid, the small tube containing it is now dropped in, with its sealed end undermost, and the combustion tube is filled with oxide of copper to about one inch of its extremity. If the substance is a liquid, the bulb in which it is contained is scratched by a file at the

Fig. 52.



middle of its neck, which is broken across when introduced into the combustion tube, as represented in *fig. 52.*, both bulb and neck being allowed to slide down the tube. If two bulbs are used, the first is placed about one inch from the closed end of the combustion tube, and the other two or three inches farther up. The oxide of copper having been introduced, the chloride of calcium tube and the potash apparatus are connected with the combustion tube in the usual manner. (page 458.)

When the oxide of copper in the anterior portion of the tube is brought to a red heat, a piece of glowing charcoal is held near the bulb containing the liquid, to expel a portion of the latter and convert it into vapour. The heat applied to the bulb is gradually increased during the whole combustion; but this must be done with great caution to prevent a sudden rush of vapour, which would in all probability render the analysis worthless. It is advisable to keep a few

pieces of red-hot charcoal near the closed point of the combustion tube, that none of the liquid may distil and be condensed there. At the termination of the combustion, a current of air is sucked through the apparatus, in the same manner as in the combustion of fixed substances.

Combustion by means of a mixture of oxide of copper with chlorate of potash.—According to M. Dumas, the carbon of an organic substance is never completely burned by oxide of copper alone, partly owing, he supposes, to the formation of a small quantity of carburet of copper with the reduced metal, and to the deposition here and there of particles of carbon which are not burned by the current of air sucked through at the end of the operation. By introducing into the closed end of the tube about two inches of a mixture consisting of one part of chlorate of potash with eight parts of oxide of copper, this source of error may be prevented to a great extent. Pure oxygen thus comes to be disengaged at the end, in which the carbon burns perfectly.

In this operation, as well as when a substance which contains a considerable proportion of nitrogen is analyzed by the ordinary method, the gas which passes through the potash apparatus becomes there saturated with moisture, which it carries away, and thus causes a deficiency in the amount of carbon. To avoid this error, a small tube, open at both ends, containing fragments of sticks of potash, is annexed to the farther extremity of the potash apparatus. The potash in that tube assumes all the water taken up by the gas, together with any trace of carbonic acid which might possibly escape the potash ley. This tube and the potash apparatus are weighed together both before and after the combustion.

Combustion by means of chromate of lead.—From the completeness with which organic bodies are burned by means of chromate of lead, that material, there is reason to believe, will supersede the use of oxide of copper to a great extent. It is obtained by precipitating the acetate or nitrate of lead by bichromate of potash, and washing the precipitate carefully with distilled water. When dry, the chromate must be

strongly calcined till it begins to melt, and be afterwards reduced to a very fine powder.

One great superiority which chromate of lead possesses over oxide of copper, is in the absence of all hygrometric property; and the trace of water absorbed by the substance, while being mixed with the chromate, is very easily removed by the exhaustion.

When chromate of lead is employed, the combustion tube need not be longer than eight inches. A moderate heat is sufficient until towards the end of the process, but the heat should then be increased considerably, so as to fuse the chromate, and thus evolve pure oxygen. The increased heat renders it necessary to protect the tube by wrapping around it a thin sheet of copper, kept in its place by a few rings of iron wire. A small tube, containing fragments of sticks of potash, should be annexed to the potash apparatus, to retain the moisture carried away by the gas as the latter passes through the ley.

DETERMINATION OF NITROGEN.

The nitrogen contained in organic bodies may be estimated in three different ways: first, by collecting the whole amount in the free state and measuring its volume; second, by determining the relation which exists between the nitrogen and carbonic acid gases produced by the combustion, having made a previous estimation of the carbon; and third, by converting the whole nitrogen into ammonia, which is weighed as the ammonio-chloride of platinum, or that compound is converted into metallic platinum, which is weighed.

It is unnecessary to state more than the outlines of the first two of these processes, as they are now likely to be superseded by the third.

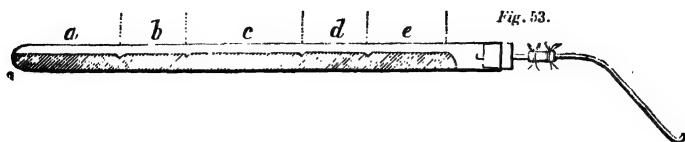
1. When the whole nitrogen is collected in the free state, a combustion tube about twenty-four inches in length is used, five or six inches of which from the closed end are filled with carbonate of copper; above this are placed two inches of pure oxide of copper; next, about six inches of the mixture

of the substance with oxide of copper; then another layer of oxide, of which three inches may be the rinsings of the mortar, and three inches pure oxide; and lastly, about five inches of metallic copper, procured by reducing the oxide by hydrogen gas. The object of introducing the metallic copper is to decompose any compound of nitrogen and oxygen which may be produced during the combustion. To get rid of the air in the tube, the latter is alternately exhausted of its air by an air-pump, and filled with carbonic acid by applying heat to one half of the carbonate of copper. These operations are continued until all the air is withdrawn, and the tube is filled with pure carbonic acid gas, which is ascertained by collecting a little of the gas at the mercurial trough in a jar which contains a solution of caustic potash: if the absorption of the gas by the alkali is complete, all the air has been withdrawn.

The metallic copper and oxide in the anterior portion are first heated, and afterwards the mixture, the evolved gases being collected in a graduated mercurial jar half full of a strong solution of caustic potash. When the substance is completely burned, the remaining half of the carbonate of copper is heated to evolve carbonic acid gas, and thus drive all the nitrogen which remains in the tube forward into the receiver. The volume of the gas not absorbed by the potash, which is pure nitrogen, is then observed, and its weight calculated, the necessary corrections being made for temperature and pressure.

2. In the second method adverted to, the nitrogen is determined by observing the relation which exists between the carbonic acid and nitrogen gases produced by the combustion. This method is applicable to those compounds only in which the nitrogen is contained in a larger proportion than one equivalent to nine equivalents of carbon. Commonly, the evolved gas is collected at different stages of the combustion in several small graduated tubes, but it is more convenient and accurate to collect the whole gas in a single jar, which may be done in the following manner:—The first four inches of a combustion tube, twenty inches in length, is filled with

a mixture of oxide of copper with one half of the substance to be analyzed, of which about seven grains in all may be

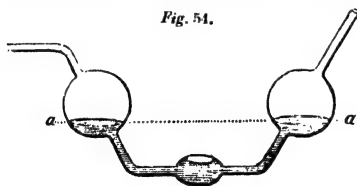


used. Next to this is placed three inches of pure oxide of copper *b*; then five inches of the mixture of oxide of copper with the remainder of the substance *c*; again, three inches of pure oxide *d*; and lastly, four inches of metallic copper *e*, obtained by reduction from the oxide by hydrogen. Heat is first applied to the metallic copper and the adjoining oxide, and afterwards to the oxide in *b*. When these portions are heated to redness, heat is applied to the mixture in *a*, beginning at the closed end, and proceeding gradually upwards until the portion of the substance there is completely burned, the gases which are formed being allowed to escape. By this means, all the air of the tube is expelled. The mixture in *c* is then heated by portions of half an inch at a time, commencing at the part nearest the closed end of the tube, all the gases which are produced being collected in a graduated jar at the mercurial trough. When the combustion is terminated, the volume of the mixed gases collected is observed; a strong solution of caustic potash is introduced into the jar, by means of a bent pipette, to absorb carbonic acid, and the volume of the residuary nitrogen is noticed. The atoms of nitrogen and carbon in the substance analyzed are in the same relation to each other as the volumes of the nitrogen and carbonic acid gases; hence, having determined the weight of the carbon by a previous experiment, the weight of the nitrogen may be obtained by calculation.

3. The third method, that in which the nitrogen is estimated by converting it into ammonia, is applicable to all azotized organic substances, excepting those in which the nitrogen exists in the form of nitric acid. The material employed is either a mixture of one part of hydrate of soda

and two of lime, or one part of hydrate of potash and three of lime: the former mixture is preferable, not being so hygrometric as the latter. The mixture is conveniently prepared by adding the proper quantity of lime to a concentrated solution of the alkali, the strength of which has been ascertained by an alkalimetical experiment, and evaporating the mixture to dryness; or it may be made by mixing the two materials in powder intimately in a warm mortar. To have a measure of the quantity of alkaline mixture necessary, it is introduced into the combustion tube, so as to fill the latter to about three or four inches of its open end; the mixture with the weighed substance is then made in a warm and dry porcelain mortar, and introduced into the tube. From five to eight grains of the substance may be operated on. The mortar is rinsed out with an additional quantity of the mixture of alkali and lime, and the rinsings are added to the mixture in the tube, placing above the whole (when the potash mixture is used) a little asbestos, to prevent the projection of any particles of the alkali. If the substance is a volatile liquid, it may be contained in small bulbs similar to those employed in the combustion of such bodies by oxide of copper. (page 463.) Attached to the combustion tube,

Fig. 54.



by a perforated cork, is a three-bulbed apparatus, represented in *fig. 54.*, of the scale of a quarter of an inch to an inch, and which is filled up to *a* with pure hy-

drochloric acid, of specific gravity 1.130. To ascertain whether the connection of this apparatus with the combustion tube is air-tight, the heat of the hand is applied to the bulb next the tube: if the liquid rises in the opposite bulb, and does not return to its former level so long as the heat of the hand is applied, the connection is perfect. Heat is then applied to successive portions of the tube, commencing at the anterior extremity. When the whole length of the tube has been heated, and the combustion seems to be complete (indicated by the whitening of the mixture, which is blackened at

first), air is sucked through the apparatus, as in the ordinary combustion by oxide of copper; the hydrochloric acid in the bulbs is poured out into a porcelain bason; and the bulbs are washed, first with a little water, then with a mixture of alcohol and ether, and lastly, with pure water. From one ounce to one ounce and a half of liquid may be used for that purpose. To the mixture of hydrochloric acid with the washings of the bulbs, a solution of pure chloride of platinum is added in slight excess, and the whole is evaporated to dryness. The dry residue of evaporation is treated with a mixture of two volumes of strong alcohol and one volume of ether: if this affords a yellow solution, an excess of chloride of platinum has been added, and the ammonio-chloride of platinum may be collected on a weighed filter, dried and weighed. To control the weighing, the ammonio-chloride is calcined, in order to convert it into metallic platinum, which is also weighed: 177 parts of nitrogen are indicated by 2,788 parts of the ammonio-chloride, and by 1,233 of metallic platinum.

To ensure the absence of any ammonio-chloride of platinum in the chloride employed in the operation, the solution of the chloride should be evaporated to dryness, and the residue redissolved in a mixture of alcohol and ether. MM. Will and Varrentrapp, to whom we are indebted for this valuable process, state that substances containing cyanogen evolve all their nitrogen as ammonia in this operation, and that it is inapplicable to those bodies only the nitrogen of which exists in the form of nitric acid.

A P P E N D I X.

APPENDIX.

1. NOTE ON THE PURIFICATION OF HYDROCHLORIC ACID. (p. 19.)

Hydrochloric acid is very rarely met with in commerce free from arsenic, the presence of which impurity considerably interferes with the applications of this acid in analysis. According to M. Büchner, the arseniferous hydrochloric acid may be rendered completely free from arsenic by digestion, with the aid of heat, with copper filings, and distillation.

2. PROCESS FOR THE COMPLETE ANALYSIS OF CRUDE POTASHES.

A complete analysis of a sample of crude potashes is often requisite for the exact commercial valuation of that article: the mere estimation of the alkali by an alkalimetric process is insufficient, in consequence of the occasional presence of caustic soda and carbonate of soda. The ingredients whose amounts should be determined are the following: —

Water,
Carbonate of lime,
Insoluble siliceous earth,
Sulphate of potash,
Chloride of potassium,
Carbonate of soda,
Silica, in combination with alkali,
Caustic soda (as a hydrate),
Carbonate of potash.

1. The *water* is estimated in the usual way, by simply heating a weighed quantity to dull redness in a platinum crucible (covered so as to avoid the access of carbonic acid from the fire), and ascertaining the loss which the substance thereby experiences in weight. The one equivalent of water, in combination with the caustic alkali present, cannot be expelled by ignition, but may be

determined by calculation, when the amount of caustic alkali present is estimated.

2. The *carbonate of lime* and *insoluble siliceous earth* remain undissolved when the substance is digested in water, and may be collected on a filter and weighed. The carbonate of lime and siliceous earth may be separated by acetic acid, which dissolves the former, and leaves the latter undissolved.

3. The liquid filtered from the carbonate of lime and siliceous earth may be used for the estimation of the *sulphate of potash* and *chloride of potassium*. The solution is supersaturated with pure nitric acid, and divided into two equal parts by means of an alkalimeter; pure chloride of barium is added to one portion, to precipitate sulphate of barytes (see p. 405.); and to the other portion nitrate of silver is applied, to precipitate chloride of silver. (See p. 412.) The weights of the sulphate of potash and chloride of potassium required are deduced by calculation from the weights of the sulphate of barytes and chloride of silver.

4. The *entire quantity of alkali existing as caustic alkali, alkaline carbonate, and alkaline silicate*, is next estimated by the ordinary alkalimetric process, sulphuric acid being the acid employed for this purpose: the solution of the potashes must be filtered before being tested. (p. 305.)

5. The object of the next operation is *the determination of the presence and proportion of soda* in the potashes. The neutral liquid obtained in the alkalimetric experiment is mixed with a little hydrochloric acid, evaporated to *dryness*, and the residue is calcined and carefully weighed. This residue consists of silica, the sulphate of potash, and chloride of potassium, originally present in the potashes, and sulphate of potash, with perhaps sulphate of soda, formed by the neutralization of the alkali with sulphuric acid. After being weighed, the mass is digested in water, and the *silica* which remains undissolved is collected and weighed. The united weights of the silica, and sulphate of potash, and chloride of potassium originally present, are deducted from the weight of the dry residue: the remainder is the weight of the alkaline sulphates formed by the neutralization with sulphuric acid. The relative proportions of sulphuric acid and the mixed bases being known, that of potash and soda in the base may be obtained by calculation, as described at p. 304. The sulphuric acid united with the mixed bases is of course the quantity applied by the alkalimeter in the fourth operation.

6. The only remaining operation is the estimation of the *caustic alkali*, by means of chloride of barium and the alkalimeter, as described at p. 311. If both a caustic alkali and soda, in some form or other, are present, the caustic alkali is to be considered as soda; *caustic potash*, however, may be present likewise, in which case the sample contains no carbonate of soda or other *salt* of soda, as such compounds are decomposed, when in solution, by caustic potash, with formation of corresponding salts of potash and caustic soda. The caustic alkali is in combination with one equivalent of water.

The conception of this course of analysis may be somewhat facilitated by the following illustration:—

1. 50 grains of the crude potashes afforded 1·5 gr. of *water*, or 3·0 per cent.

2. 50 grains, when digested in water, left undissolved 1·25 gr. of *carbonate of lime*, with a trace of *silica*; or 2·5 per cent.

3. The liquid filtered from the carbonate of lime afforded, in the third operation, 1·97 grains of sulphate of barytes, and 1·8 grains of chloride of silver. These amounts are equivalent to 1·5 grains of sulphate of potash (or 6·0 per cent.), and 0·95 gr. of chloride of potassium (or 3·8 per cent.).

4. 100 grains dissolved in water, and the solution filtered, required, for complete neutralization, 40 measures of the diluted sulphuric acid used in testing soda-ash: these 40 measures for *soda* are equivalent to 60 measures for *potash*, and contain 51·1 gr. of absolute sulphuric acid.

5. The liquid obtained in the last operation left, on evaporation to perfect dryness, a residue which weighed 118·9 grains; the *silica* of which amounted to 1·1 gr. When the silica and the chloride of potassium and sulphate of potash originally present are deducted from this residue, there remain 108·0 grains, consisting of alkaline sulphates formed in the alkalimetric operation by the application of 51·1 gr. of real sulphuric acid: the mixed bases in the 108·0 grains amount, therefore, to 56·9 grains. Now 1 part of soda unites with 1·277 parts of sulphuric acid, to form neutral sulphate of soda; and 1 part of potash unites with 0·846 of sulphuric acid, to form neutral sulphate of potash: the difference between the two proportions of sulphuric acid is therefore 0·431 to 1 of base. From these data the proportions of potash and soda in the 56·9 of mixed bases are thus calculated: $56·9 \times 0·846 = 48·1$; $48·1 - 51·1$ (the sulphuric acid applied) $= 3·0$; and $3·0 \div$

0.431=6.9, which is the amount of *soda* in the 56.9 of mixed bases, leaving 50.0 of potash. These amounts of potash and soda may be partly in the caustic state and partly as carbonate; and considering the 1.1 gr. of silica to be combined with one equivalent of potash, 1.2 gr. of potash is as silicate.

6. By the process for estimating the *caustic alkali* described at p. 311., an alkali is found to be present in the caustic state equivalent to 1.8 measures of the soda test acid per cent.; and since the potashes is found to contain 6.9 of soda per cent., therefore the whole of the caustic alkali is soda, and 5.1 of soda is in the state of carbonate. The 1.8 of caustic soda is combined with 0.5 of water (one equivalent).

Of the 50.0 parts of potash in the state of carbonate and silicate, 1.2 parts are to be considered as in combination with silica. Therefore 48.8 parts of potash exist as carbonate, being combined with 22.7 parts of carbonic acid.

The result of the analysis is therefore the following:

| | | | | | |
|---|---|---------------|---|---|---------------|
| Water expelled by ignition | . | . | . | . | 3.0 per cent. |
| Carbonate of lime, with a trace of silica | . | . | . | . | 2.5 " |
| Chloride of potassium | . | . | . | . | 3.8 " |
| Sulphate of potash | . | . | . | . | 6.0 " |
| Carbonate of potash | { | Potash | . | . | 48.8 " |
| | | Carbonic acid | . | . | 22.7 " |
| Carbonate of soda | { | Soda | . | . | 5.1 " |
| | | Carbonic acid | . | . | 3.5 " |
| Caustic soda (hydrated) | { | Soda | . | . | 1.8 " |
| | | Water | . | . | .5 " |
| Silicate of potash | { | Potash | . | . | 1.2 " |
| | | Silica | . | . | 1.1 " |
| | | | | | <hr/> |
| | | | | | 100.0 |

3. PROCESS FOR THE ANALYSIS OF ORES OF MANGANESE.

The commercial value of ores of manganese, as a source of chlorine, is dependent not only on their proportion of peroxide of manganese, but likewise on that of other oxides which are usually present, and which consume a certain quantity of acid without eliminating chlorine. The smaller the proportion of these other oxides, of course the more valuable is the sample. An accurate valuation of an ore of manganese, therefore, must embrace the proportion of peroxide, together with the proportion of acid

required for working the ore, or, what amounts to the same thing, the respective quantities of the other oxides which consume acid without affording chlorine.

The following mode of examining ores of manganese, with this view, will be found to afford results of sufficient precision for practical purposes.

1. The *water* in the sample is determined by heating 50 grains in a porcelain capsule to a temperature somewhat above the boiling point of water, so long as the sample loses weight.
2. The proportion of *peroxide of manganese* in the sample is estimated in the usual way by means of protosulphate of iron. (p. 332.)
3. 25 or 50 grains of the sample are dissolved in hydrochloric acid, the solution is evaporated to dryness, and the residue is treated with diluted hydrochloric acid. The *silica* which remains undissolved is collected on a filter, washed, dried, and weighed.

When the united proportions per cent. of the silica, water, and peroxide of manganese are deducted from 100, the remainder is the per-centage of peroxide of iron and protoxide of manganese, with sometimes a small quantity of alumina.

To estimate these bases, the solution filtered from the silica may be mixed with an excess of solution of caustic potash, warmed, and filtered from the precipitate of peroxide of iron and protoxide of manganese then produced: the *alumina* in the filtered liquid is precipitated by the addition of an excess of muriate of ammonia. (See p. 322.) After being washed, the precipitate of peroxide of iron and protoxide of manganese is dissolved in hydrochloric acid, the solution is neutralized with ammonia, and the *peroxide of iron* is precipitated by benzoate or succinate of ammonia. (See p. 336.) The *protoxide of manganese* in the ore may be estimated as loss; or it may be determined directly, in the usual way (p. 330.), by operating on the liquid filtered from the precipitate of benzoate or succinate of iron, and deducting from the whole amount of protoxide of manganese, thus obtained, the quantity equivalent to the peroxide of manganese in the ore, as the peroxide is reduced to protoxide (or protochloride) when dissolved in hydrochloric acid.

1 part of *peroxide of manganese* consumes 4.55 parts of muriatic acid of 36° Twad. (1.180); or, 2.27 parts of sulphuric acid of 169° Twad. (1.845), with 1.82 parts of salt.

1 part of *protoxide of manganese* consumes 2·76 parts of muriatic acid of 36° Twad. ; or 1·4 parts of sulphuric acid of 169° Twad., with the proportional quantity of salt.

1 part of *peroxide of iron* consumes 3·80 parts of muriatic acid of 36° Twad. ; or 1·87 parts of sulphuric acid of 169° Twad., with the proportional quantity of salt.

1 part of *alumina* consumes 4·38 parts of muriatic acid of 36° Twad. ; or 2·16 parts of sulphuric acid of 169° Twad., with the proportional quantity of salt. /

4. REFRACTION OF NITRE.

The impurities with which commercial nitre is usually contaminated, are water, chloride of sodium, alkaline sulphates, and occasionally a small quantity of insoluble earthy matter. The total amount of these impurities in 100 parts of a sample of nitre is technically termed the "refraction" of that sample.

1. An ingenious, but, probably, not very accurate, method of refracting nitre, consists in digesting a known weight of the powdered sample in a *cold saturated solution* of nitre, which possesses the property of dissolving chloride of sodium and alkaline sulphates, although it does not dissolve more nitre. After digestion for some time, the liquid is drained off, and the undissolved crystals are dried, first, by pressure between folds of filtering paper, and afterwards by the application of a moderate heat. But as the quantity of nitre which water is capable of dissolving varies considerably with the temperature, it is necessary to operate, at the same time, and in precisely the same circumstances, upon the same weight of pure dry nitre. The difference found at the end of the experiment between the two quantities represents the proportion of water and of foreign salts in the sample. The insoluble earthy matter is determined by another operation, by simply dissolving a known weight of the sample in water, filtering the liquid, and washing, drying, and weighing the insoluble matter on the filter.

2. The most usual method of refracting nitre consists in determining, 1°, the amount of *water* lost by exposure to a moderate heat; 2°, the amount of *insoluble matter*; 3°, the amount of chloride of silver precipitated by the application of nitrate of silver, from which the *chloride of sodium* is calculated; and 4°, the amount of sulphate of barytes precipitated by the application of chloride of barium, from which the amount of *sulphate of*

potash (or sulphate of soda) is calculated. The loss is considered as pure nitre.

5. Neither of these methods give precise results, the latter being imperfect from affording no means of determining how much of the base is soda. If, in addition to the operations of the second process, the nitric acid is estimated directly by distilling the nitrate with sulphuric acid, after addition of sulphate of silver and filtering (as described at p. 431.), then all the data necessary for calculating the quantity of soda in the base are obtained. For an example of a calculation of this kind, see p. 304., and also p. 475.

5. VALUATION OF GUANO.

Although the composition of guano is highly complicated, many samples of this substance containing not less than twenty distinct ingredients, yet the value of this article as a manure may be determined with precision by a few simple and easily executed experiments.

The valuable constituents of guano are alkaline and earthy phosphates, and nitrogen, in a form capable of elimination as ammonia. Some of the remaining constituents, namely, the alkaline sulphates and muriates, possess a very small value compared with the phosphates and ammonia; while others, as water and sand, are altogether worthless.

1. The estimation of the *ammonia*, already formed as an ammoniacal salt,* together with that capable of being formed during the spontaneous decomposition of the azotized organic matter, is effected by the following process. A known weight of the sample (not more than twenty grains), is introduced into an ordinary test-tube, of about five inches in length and three quarters of an inch in diameter. A few inches of sticks of potash are placed in the tube, which is immediately connected, by means of a sound perforated cork, with the apparatus figured at page 469., containing hydrochloric acid of about 1.1 sp. gr. The extremity of this apparatus attached to the test-tube is bent downwards a little, to allow of the inclination of the test-tube. The apparatus having been proved to be air-tight, heat is applied to the test-tube

* The *free ammonia* in guano is never more than a mere trace, scarcely appreciable by the balance. It is also a mistake to suppose that carbonate of ammonia is present in guano to any appreciable extent. The odour of free ammonia exhaled by guano seems to arise from the decomposition of the sulphophosphate of ammonia.

by means of a spirit-lamp; the heat should be rather moderate at first, to prevent a too rapid disengagement of gas; but, towards the end of the operation, the tube is heated strongly, throughout its length, by two spirit-lamps with large flames. Care should always be observed to keep the tube hot enough in the higher part, to prevent the condensation of water, otherwise a drop might fall down the tube and give rise to a fracture, by coming in contact with a part strongly heated. When the disengagement of ammonia is nearly complete, the mass in the tube loses its semi-fluid appearance, and becomes solid; and, usually, a gas passes through the hydrochloric acid without being absorbed. This gas, which is light carburetted hydrogen, may completely drive the ammoniacal gas from the tube into the hydrochloric acid, but it is always advisable to ensure the complete absorption of the ammonia by other means. The heat is continued for about five minutes after the mass has become solid, and then withdrawn; the liquid in the bulbed tube is allowed to rise to a higher level in the bulb nearer the test-tube than in the other bulb; and an opening is made at the closed extremity of the test-tube, by allowing a drop of cold water to fall upon it while strongly heated; air is immediately drawn through the apparatus by suction at the opposite extremity.

For ordinary purposes, sufficiently exact results are obtained by simply evaporating the acid solution of muriate of ammonia to perfect dryness in a bason at a moderate heat, and weighing the dry residue of muriate of ammonia, 1 part of which represents 0.315 of ammonia. After being weighed, the muriate of ammonia may be sublimed, in order to separate any fixed matter which might accidentally be present, which is weighed and deducted from the muriate of ammonia.

But the weight of the ammonia is determined with more accuracy by mixing the acid solution of muriate of ammonia with a slight excess of chloride of platinum, and proceeding further as directed at page 469.

2. If the ammonia is estimated, the determination of the *water* is not essential to the valuation of a sample of guano. A convenient means of estimating this ingredient is by placing a known weight of the sample upon a piece of bibulous paper over a surface of oil of vitriol, the whole being covered with a bell-jar, and made air-tight at bottom. (See p. 299.)

3. The estimation of the *phosphate* and *sand* may be made in the following manner. A known weight (say 50 grains) of the

sample is calcined in a porcelain or platinum crucible until the organic matter is completely burned away (no black particles being perceptible in the residue), and the remaining ash is weighed. This ash consists of alkaline and earthy phosphates, sand, and, usually, common salt and alkaline sulphates. If the calcination is conducted at rather a high temperature, a little of the common salt may have been volatilized, but that need not affect the valuation of the sample.

After being weighed, the ash is digested in water, whereby the *alkaline salts* are removed, and the portion of the ash undissolved by water is collected on a filter, washed, dried, and weighed. The loss in weight, produced by the washing, is the *alkaline salts*. The *phosphoric acid* contained in these alkaline salts may be precipitated from the aqueous solution by applying sulphate of magnesia with ammonia, and be weighed as phosphate of magnesia. (See page 424.)

To obtain the proportion of *sand*, the ash, after being treated with water, dried, and again weighed, is digested in diluted hydrochloric acid, which soon dissolves the phosphates of lime and magnesia entirely, and leaves the sand undissolved, which is collected on a filter, washed, dried, and weighed. The phosphoric acid in the acid solution is estimated by the process described at page 427. (by applying perchloride of iron, ammonia, hydrosulphate of ammonia, &c.).

Some samples of guano, of recent importation, contain, in addition to the ingredients above mentioned, a considerable quantity of gypsum (sulphate of lime).

/ 6. NOTE ON THE ANALYSIS OF SOILS.

The complete analysis of a soil is, generally, about the most complicated of all analytical operations. The course to be pursued in the complete qualitative analysis of a soil is the same as prescribed in the third division of this work, on Systematic Qualitative Analysis; separate examinations being made of the portions soluble in water and soluble only in acids. Attention should be especially directed to the presence of *phosphoric acid*, which should be sought both in the part soluble in water and in that soluble only in acids. The means of detecting phosphoric acid are pointed out at page 127. The presence of *silicic acid*, in a state soluble in water or dilute acids is also worthy of especial examination.

Separate examinations should not only be made of the portions

varying from each other in their relation to solvents, but of the parts differing in their mechanical state. To separate the finer from the coarser constituents, the soil may be dried and passed through sieves of different degrees of fineness: or else, the separation may be effected by affusion of water, and decantation, after the grosser portions of the soil have subsided, but while the finer portions still remain in suspension; this operation being repeated as often as may be deemed necessary. When the latter mode is practised, of course the soil is first digested for some time in water, to remove all the matters soluble in that liquid, the aqueous solution being examined apart, both qualitatively and quantitatively. The analysis of this aqueous solution is much the same as that of a saline mineral water. (page 442.)

The general character of a soil may often be determined by a few simple experiments, without the trouble of a complete quantitative analysis. Thus the presence or absence of carbonates is ascertained by observing whether effervescence is produced on the application of hydrochloric acid; that of alkaline sulphates and chlorides, by observing whether or not the water which has been digested on the soil contains sulphuric acid or chlorine. A small quantity of sulphuric acid, however, may be present in the aqueous solution, in the form of sulphate of lime; in which case oxalate of ammonia produces a precipitate of oxalate of lime. Phosphoric acid should always be sought by the method described at p. 127. The presence of ammonia, or of nitrogen capable of producing ammonia, is detected by the odour of ammonia disengaged when the soil is heated with strong potash ley, or with moistened fragments of potash.

A cursory quantitative analysis of a soil or manures conducted after the plan of the analysis of guano in the preceding note, often affords results of sufficient accuracy for all practical purposes. The quantity of earthy carbonates is determined by the process described at page 435.

7. ANALYSIS OF ASHES OF VEGETABLES.

The bases usually found in ashes of plants are — potash, soda, magnesia, lime, peroxide of iron, and occasionally oxide of manganese. The acids, or electro-negative bodies, associated with these bases are — phosphoric acid, sulphuric acid, silicic acid, carbonic acid (derived from the decomposition, by heat, of organic acids); and chlorine, bromine, iodine, and fluorine.

The following plan for the analysis of ashes of plants, is in most

respects the same as that recently proposed by Drs. Will and Fresenius ("Memoirs and Proceedings of the Chemical Society," Part. IX.).

1. Ashes which are entirely or for the most part soluble in hydrochloric acid, may be treated in the following manner. Fifty or sixty grains of the ash are digested in hydrochloric acid, the liquid is evaporated to dryness, and the residue is rather sharply heated, so as to render the deposited silica insoluble. (page 400.)

The dry residue is moistened with strong hydrochloric acid, the mixture is diluted with water, and poured upon a filter. The matter upon the filter is washed, dried, and weighed. It usually consists of charcoal, sand, and silica, deposited from a state of solution : by digestion in a caustic alkali, the fine silica is dissolved, while the sand and charcoal remain undissolved, and may be collected in the usual way, and weighed. If necessary, the charcoal and sand may be separated from each other by incineration.

The liquid filtered from the sand, &c. is divided, by means of an alkalimeter (page 306.), into three equal portions ; in one of which the oxide of iron, oxide of manganese, and alkaline earths, are estimated ; in another, the phosphoric and sulphuric acids ; and in another, the alkalies.

2. For the estimation of the peroxide of iron and alkaline earths, the liquid is mixed with ammonia in slight excess, which precipitates phosphate of the peroxide of iron, and either oxide of iron or an earthy phosphate. Acetic acid is next added in decided excess, to dissolve the phosphate of lime or free oxide of iron, and the undissolved phosphate of iron is collected on a filter (after warming the liquid), washed, ignited strongly, and weighed. After being heated to redness, the phosphate of iron contains 41.6 per cent. of oxide of iron. The lime in the filtered liquid is estimated as oxalate in the usual way (page 315.) ; and to the solution filtered from the oxalate of lime, ammonia and phosphate of soda are applied, to precipitate magnesia. (page 318.) If the liquid filtered from the phosphate of iron contains peroxide of iron (in which case the absence of earthy phosphates may be inferred), the liquid, before the lime is precipitated, is rendered neutral or slightly ammoniacal, and iron, and manganese, if present, are then precipitated as sulphurets by hydrosulphate of ammonia. (For the modes of separating iron and manganese from each other, see page 336.) From the filtered ammoniacal solution, lime and magnesia are separated in the usual way.

3. To the portion of the solution filtered from the sand, &c.,

chloride of barium is added, for the purpose of separating and estimating sulphuric acid. (page 405.) The liquid filtered from the sulphate of barytes is subjected to the process for estimating phosphoric acid described at page 427.

4. To estimate the alkalies in the ash, the remaining portion of the solution filtered from the sand, &c. is mixed with excess of barytes-water, the mixture is heated and filtered, and the precipitate on the filter is well washed. The excess of barytes in the filtered liquid is precipitated by the addition of carbonate of ammonia and some free ammonia : after filtration, the solution is evaporated to dryness, the residue is calcined to expel ammoniacal salts, and the fixed alkaline chlorides remaining are weighed. A trace of magnesia generally remains undissolved when these chlorides are dissolved in water. By determining their proportion of chlorine, that of the potassium and sodium may be deduced by calculation. (See page 305.)

If hydrochloric acid has but little action on the ash which is the subject of examination, the alkali should be estimated by one of the processes described at page 404., the ash being strongly calcined with either quick-lime or caustic barytes.

5. The carbonic acid in the ash is estimated by the process described at page 435., and the chlorine by digesting the ash in hot water slightly acidulated with nitric acid, and precipitating the chlorine as chloride of silver.

Ashes which are acted on with difficulty by hydrochloric acid may be heated, in a platinum or silver capsule, with strong potash or soda ley : the silicates are thereby acted on, and for the most part dissolved, while the sand remains undissolved.

8. METHOD OF CALCULATING THE ATOMIC CONSTITUTION OF A BODY FROM ITS PER-CENTAGE COMPOSITION.

The result of a quantitative analysis is first stated in the composition of 100 parts of the body analyzed. If the compound possesses a definite composition, that is, if it is not a mere mechanical mixture of its constituents, there remains to be discovered the *atomic constitution* of the substance, or *the number of equivalents of each constituent contained in one equivalent of the compound*. The equivalent of a compound body is the sum of the equivalents of its constituents : if, therefore, the equivalent of a compound be 100, the per-centage amount of any one of the constituents must either be the single equivalent number of that constituent, or else a simple multiple of the equivalent ; and consequently, when the per-centage

is divided by the equivalent, it should give the number of atoms of the particular constituent contained in one atom (100) of the compound. In like manner, if the equivalent of a compound be more or less than 100, the per-centage amounts of the ingredients, when divided by the respective single equivalent numbers, give the proportions in which the atoms exist with relation to each other, instead of the actual number of atoms, which last is then obtained by a simple calculation. This will be more obvious by an illustration. The analysis of crystallized sulphate of nickel gives in 100 parts —

| | | | | | |
|-----------------|---|---|---|---|--------|
| Oxide of nickel | . | . | . | . | 26·95 |
| Sulphuric acid | . | . | . | . | 28·37 |
| Water | . | . | . | . | 44·68 |
| | | | | | <hr/> |
| | | | | | 100·00 |

Now the equivalent of oxide of nickel (taking the whole number on the hydrogen scale) is 38; the equivalent of sulphuric acid is 40; and the equivalent of water is 9. Then the per-centage of oxide of nickel, 26·95, divided by the equivalent of oxide of nickel, 38, gives the number ·709; the per-centage of sulphuric acid, 28·37, divided by the equivalent of sulphuric acid, 40, gives the number ·709; and the per-centage of water, 44·68, when divided by the equivalent of water, 9, gives the number 4·964.

The proportions, therefore, of the atoms are —

0·709 of oxide of nickel,
0·709 of sulphuric acid, and
4·964 of water ;

Numbers which correspond to —

1 atom of oxide of nickel,
1 atom of sulphuric acid,
7 atoms of water.

An analysis of sugar gave, as the composition of that substance, in 100 parts —

| | | | | | | |
|----------|---|---|---|---|---|---------|
| Carbon | . | . | . | . | . | 42·4 |
| Hydrogen | . | . | . | . | . | 6·5 |
| Oxygen | . | . | . | . | . | 51·1 |
| | | | | | | <hr/> |
| | | | | | | 100·0 ; |

which quantities of carbon, hydrogen, and oxygen, when divided by the respective equivalents of these elements, give —

7.06 atoms of carbon,
 6.50 atoms of hydrogen, and
 6.38 atoms of oxygen.

The nearest corresponding whole numbers (allowing for the usual slight excess of hydrogen) being 12 of carbon, 11 of hydrogen, and $1\frac{1}{4}$ of oxygen.

9. METHODS OF TAKING THE SPECIFIC GRAVITY OF BODIES.

By the specific gravity or density of a substance, is understood the relation which exists between its volume and its weight. If one body is found to possess twice the weight of another body, the bulks of the two being equal, one is said to have twice the density or specific gravity of the other, and thus in proportion; so that, the volumes being equal, the densities of bodies are directly as their weights; or the weights being equal, the densities are inversely as the volumes. For convenience in comparison, *the densities of solids and liquids are referred to pure water, and the densities of gases to dry air, as the standards of unity*; hence the number representing the specific gravity of a solid or liquid is the number of times it is heavier than water, and the specific gravity of a gas or a vapour is the number of times it is heavier than air, both being taken at the temperature of 60° Fahr., and under a pressure of 30 inches of the barometer.

In taking the density of a body, the experiment is to ascertain either the weight of a given volume, or the volume of a given weight, and then to compare the weight with that of an equal bulk of the standard; that is, either of water or of air.

1. *Liquids*. — To take the specific gravity of a liquid, it is brought to the temperature of 60° Fahr., and introduced into a counterpoised phial or flask, which is capable of holding, when quite full, exactly 1000 grains of distilled water at the temperature of 60° Fahr. The bottle being counterpoised, the liquid is then weighed. As the bottle holds 1000 grains of water, the weight of the liquid gives its specific gravity. Thus, if the liquid operated on is proof spirit, it would be found to weigh very nearly 918.6 grains; if oil of vitriol, it would weigh 1845 grains; and if mercury, it would weigh 13,500 grains; which numbers are the densities of these liquids, water being taken as 1000; or if water is taken as 1, the decimal point is advanced three figures to the left.

Notwithstanding the simplicity of the above method, it is not

generally followed, from the inconveniently large size of a bottle holding so much as 1000 grains. A much smaller bottle is preferred, weighing from 100 to 200 grains, and holding, when full, from 200 to 300 grains of water. It should be provided with a stopper formed from a piece of thermometer tube, the bore in which allows the excess of liquid to exude when the stopper is applied to the filled bottle. The weight of the flask in a perfectly clean and dry state, and also its weight when full of distilled water at 60°, having been observed, the weight of water it holds is ascertained. Then by deducting the weight of the bottle from its weight when full of the liquid whose density is to be taken, the weight of the latter is obtained, and its density may be calculated, by the rule, — As the weight of water is to the weight of liquid, so 1 is to the density of the liquid. That is, the density of the liquid is obtained by dividing its weight by the weight of the water.

2. *Solids heavier than water.* — The solid whose density is required is first weighed in air, and afterwards (if insoluble) in distilled water at 60°, being suspended from the pan of the balance by a fibre of unspun silk. The weight of the substance in water is found to be less than in air; and the weight lost by immersion represents the weight of the bulk of water which the body displaces, according to the hydrostatic law, that the weight of a substance in any medium (such as water in the present instance) is less than its absolute weight by the weight of the bulk of the medium which it displaces; and obviously, it must displace its own bulk. We thus obtain the two data necessary to calculate the density of a solid; namely, the weight of the substance in air, and also the weight of its own bulk of water. Suppose a substance which weighs 420 grains in air to weigh 345 grains in water; then the weight lost by immersion being 75 grains, we have the proportion —

$$\text{as } 75 : 420 :: 1 : 5.6 ;$$

5.6 is therefore the density of the substance in question.

Another method of obtaining the specific gravity of an insoluble substance, is by the use of the bottle employed in taking the specific gravity of liquids. A known weight of the substance is introduced into the bottle, which is completely filled with water, and weighed. The weight of the bottle when containing both the substance and water is subtracted from the sum of the weights of

the substance in air and the bottle when containing water only; the remainder is the weight of the water which the solid displaces. For example, suppose the weight of the substance in air to be 180 grains, the weight of the bottle when filled with water 240 grains, and the weight of the bottle when containing both the substance and water 390 grains: then from 420 ($180 + 240$) subtract 390, the remainder, 30, is the weight of the volume of water displaced by 180 grains of the substance; and hence the proportion as $30 : 1 :: 180 : 6$. The specific gravity required is therefore 6.

If the solid whose density is to be taken is soluble in water, some other fluid of known specific gravity must be used, in which it is insoluble. Either oil of turpentine, alcohol, or olive oil will generally be found available. The specific gravity of the substance is then found by the following proportion, — As the density of water is to the density of the liquid used, so is the density of the substance in relation to the liquid in which it is weighed as unity, to its density compared with water as unity. If, for example, a body is found to possess the density 3, compared with olive oil as unity, then olive oil being .91 compared with water as 1, we have the proportion, as 1 (the assumed density of water) is to .91, so is 3 to 2.73, which is the specific gravity required.

3. *Solids lighter than water.* — When the solid whose density is required is lighter than water, it should be attached by means of a slender thread to a piece of a heavier solid of sufficient weight that both when together shall sink in water. The points to be determined experimentally in such a case are —

1. The weight of the light solid in air;
2. The weight of the heavy solid in air;
3. The weight of the heavy solid in water; and
4. The weight of the two together in water.

The difference between the weight of both bodies tied together in water, and the sum of their weights in air, shows the weight of the whole bulk of water displaced by both. To know how much of this is due to the heavy body, the weight of the latter in water is subtracted from its weight in air; the remainder is the weight of the water displaced by the heavy body alone; which, deducted from the entire weight of water displaced by both, leaves that displaced by the light body alone. The rule therefore is — from

the difference between the weight of the two in water and their weight in air, subtract the difference between the weight of the heavy solid in air and its weight in water; the remainder is the weight of a quantity of water equal in bulk to the light solid, from which the specific gravity of the substance may be obtained by simple proportion. As an example, suppose the following case:—

| | | | |
|--|---|----|--------|
| 1. The weight of the light solid in air | - | 12 | grains |
| 2. The weight of the heavy solid in air | - | 22 | „ |
| 3. The weight of the heavy solid in water | - | 19 | „ |
| 4. The weight of both tied together in water | - | 8 | „ |
| Then, from the weight of both in air (12 + 22) | - | 34 | grains |
| Deduct the weight of both in water | - | 8 | „ |
| | | — | „ |
| | | 26 | „ |
| And from the remainder deduct 22 — 19 = 3 | - | 3 | „ |
| | | — | |
| Which gives the weight of the bulk of water | } | 23 | „ |
| displaced by the light body alone | | | |

The following proportion then affords the specific gravity of the body:—

$$\text{as } 23 : 12 :: 1 : 0.5217.$$

4. *Gases.*—The standard of comparison to which the densities of gases and vapours are referred is air; as it would be inconvenient, from the extreme lightness of these bodies, to compare their weights with that of an equal bulk of water. From the careful experiments of Dr. Prout, it appears that 100 cubic inches of atmospheric air deprived of carbonic acid and aqueous vapour weighs 31.0117 grains, at 30 inches of the barometer, and at the temperature of 60° Fahr.; from which observation it is easy to calculate the absolute weight of any bulk of a gas from its specific gravity. Thus the specific gravity of chlorine is found to be 2.47; to find how much 100 cubic inches of that gas weigh at mean temperature and pressure, we make use of the proportion,

$$\text{as } 1 : 2.47 :: 31.01 : 76.59;$$

therefore 100 cubic inches of chlorine weigh 76.59 grains.

The simplest method of obtaining the specific gravity of a gas is the following:—The object is to ascertain the weight of a bulk of gas equal to the bulk of a known weight of air. For this pur-

pose, a light glass globe, furnished with a stop-cock, is very accurately weighed, when full of air; then exhausted of its air, by connecting it with an air-pump, and weighed in the vacuous state. The weight of the air withdrawn by the exhaustion is thus ascertained. The globe, still vacuous, is connected with a jar containing the gas which is to be weighed, at the water or mercurial trough; the jar having a stop-cock at its top, into which the stop-cock of the globe can be screwed air-tight. On gently opening both stop-cocks, a quantity of gas rushes from the jar into the exhausted globe, equal in bulk to the air withdrawn by the exhaustion, if the surface of the liquid within the jar be brought to the level of that without in the trough, and the temperature of the air and the barometric pressure have not varied during the experiment. The stop-cock being closed, the globe is detached from the jar, and weighed. The difference between its weight when containing the gas, and when vacuous, is the weight of a bulk of the gas equal to the bulk of air whose place it occupies, the weight of which has already been determined.

Suppose the globe to lose 10·33 grains by exhaustion of air, and, when exhausted, to gain 15·78 grains by admitting carbonic acid gas; then, assuming 1· as the density of air, we have the proportion,

$$\text{as } 10\cdot33 : 15\cdot78 :: 1\cdot : 1\cdot527;$$

the specific gravity of carbonic acid gas is, therefore, 1·527.

Although thus simple in principle, the operation in its details is one of extreme delicacy. From the facility with which gases undergo a change in their bulk through variations of temperature and pressure, it is obvious that if the temperature and barometric pressure vary during the course of the experiment, corrections must be made. As an illustration of the necessary corrections, suppose the bulk of air to weigh 12 grains at the temperature of 60° Fahr., and under a pressure of 30 inches bar.; and the same bulk of the gas whose density is required to weigh 20 grains, but at the temperature of 50° Fahr., and under a pressure of 28 inches bar. The points to be determined here are two:—

1. Considering the volume of the air withdrawn and the gas admitted as 1; at the observed temperatures and pressures, what would be the volume of the gas at the temperature and pressure at which the air was weighed?

And, 2., having obtained that volume, what is the corresponding increase or reduction in the *weight* of the gas?

Performed according to rules which are given in the note below*, the results of these calculations are as follow :—

(a) A volume of gas equal to 1 at 50° Fahr. is equal 1.019 at 60° Fahr.

(b) A volume of gas equal to 1.019 at 28 inches of the barometer is equal to 0.951 at thirty inches.

A volume of the gas, therefore, equal to 0.951 weighs 20 grains; a volume of air equal to 1 at the same temperature and pressure weighing 12 grains. Then, if 0.951 vol. weighs 20 grains, 1 vol. should weigh 21.03 grains : and

$$\text{as } 12 : 1 :: 21.03 : 1.75;$$

1.75 is therefore the density required.

The state of dryness of a gas is another circumstance which interferes with its volume; for which reason, due care should be taken to insure either the perfect dryness of the gas, or its complete saturation with moisture. In the latter case the temperature must be noticed and the observed volume reduced according to the proportion of aqueous vapour capable of existing in the gas at the observed temperature. The proportions of vapour by volume contained in 1 vol. of the saturated gas for temperatures between

* 1. *For changes in bulk by pressure.*—The volume which a gas should possess at one pressure may be calculated from its known volume at another pressure, by the use of the following proportion :—As the pressure to which the gas is to be corrected is to the observed pressure, so is the observed volume to the volume required. In the example in the text (b), the pressure to which the gas is to be reduced is 30 inches, the observed pressure 28 inches, and the volume 1.019. Then as 30 : 28 :: 1.019 : 0.951.

2. *For changes in bulk by temperature.*—From the very recent experiments of M. Regnault, it appears that a volume of gas expands by heat $\frac{1}{273}$ of its bulk for each degree Fahrenheit. Hence, the volume of a gas at 0° Fahr. being 1, at any higher temperature it is found by the formula $1 + \frac{t}{459}$. The determination of the volume of a gas at one temperature from its known volume at another temperature may be attained by the following formula :—Let t be the temperature Fahrenheit at which the volume of the gas is observed; t' the temperature Fahrenheit to which the volume of the gas is to be reduced; x the observed volume at t ; and x' the volume at t' required;

$$\text{Then } x' = \frac{(459+t') \times x}{459+t}$$

3. It is frequently necessary to combine corrections both for temperature and pressure. In such a case, as in the example in the text, the reduction of volume is first made for temperature, and that corrected volume is afterwards reduced according to the pressure.

40° and 80° Fahr. are expressed in the following table* (Faraday's *Manipulation*).

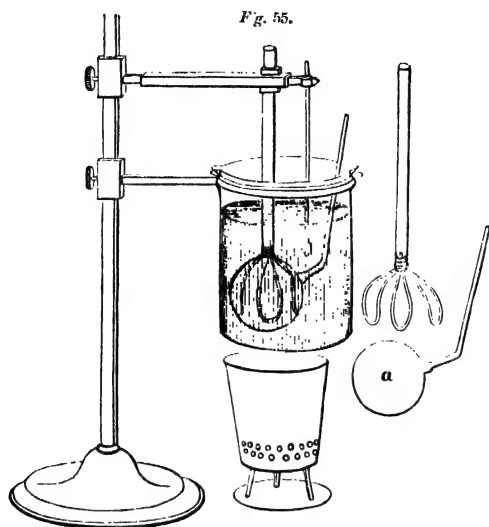
| | | | | | |
|-----|--------|-----|--------|-----|--------|
| 40° | ·00933 | 54° | ·01533 | 68° | ·02406 |
| 41 | ·00973 | 55 | ·01586 | 69 | ·02483 |
| 42 | ·01013 | 56 | ·01640 | 70 | ·02566 |
| 43 | ·01053 | 57 | ·01693 | 71 | ·02653 |
| 44 | ·01093 | 58 | ·01753 | 72 | ·02740 |
| 45 | ·01133 | 59 | ·01810 | 73 | ·02830 |
| 46 | ·01173 | 60 | ·01866 | 74 | ·02923 |
| 47 | ·01213 | 61 | ·01923 | 75 | ·03020 |
| 48 | ·01253 | 62 | ·01980 | 76 | ·03120 |
| 49 | ·01293 | 63 | ·02050 | 77 | ·03220 |
| 50 | ·01333 | 64 | ·02120 | 78 | ·03323 |
| 51 | ·01380 | 65 | ·02190 | 79 | ·03423 |
| 52 | ·01426 | 66 | ·02260 | 80 | ·03533 |
| 53 | ·01480 | 67 | ·02330 | | |

The preceding method of obtaining the density of a gas still requires a slight correction from another circumstance, when the temperature and pressure differ considerably at the time of weighing the air and at the time of weighing the gas; but one so trifling that it may, in general, be neglected. The necessity of this correction arises from the impossibility of obtaining a perfect vacuum in the globe; and the remaining small quantity of air may occupy a different space when weighed with the gas, to that which it occupied when the globe was weighed with air; and consequently, the bulk of the gas admitted into the globe is not the same as the bulk of the air withdrawn. If the amount of rarefaction of the air in the exhausted flask is observed, by means of a barometer gauge attached to the air-pump, the amount of the remaining air may be calculated when the weight of the quantity withdrawn is ascertained; then the alteration to which it would be subject in bulk by changes of temperature and pressure may also be estimated, and a due allowance made on the bulk of the gas admitted into the globe.

5. *Method of taking the density of vapours.* — Few processes of recent invention have been of more assistance in the prosecution of chemical research than the method contrived by M. Dumas for obtaining the density of the vapour of a volatile body. Neglecting the minute, but generally unnecessary, precautions requisite to insure results of mathematical accuracy, the process is briefly the

* A cubic inch of aqueous vapour corrected to the temperature of 60°, and at a pressure of 30 inches, weighs 0·1929 grains.

following :— A light glass globe (*a*, *fig. 55.*), having a capacity of from twelve to sixteen fluid ounces, is drawn out at its neck to a



narrow tube six or eight inches long, as shown in the figure ; the point of the tube is cut across with a file, and fused, but not sealed. The globe is then weighed, containing, as usual, atmospheric air, and the temperature and pressure at the time observed. To introduce a volatile liquid into the globe, the latter is warmed so as to expel a portion of its air, and the end of the beak is dipped under the surface of the liquid. As the globe cools, the air within contracts, and the liquid is sucked up. When a sufficient quantity of the liquid has entered (from 100 to 150 grains), the globe is enclosed in a sort of wire cage, as represented in the figure, and immersed in a bath of some material which can be heated to 50° or 60° above the boiling point of the substance. Either water, oil, chloride of calcium, chloride of zinc, or the fusible alloy of bismuth, tin, and lead may be used for this purpose. When the temperature of the bath rises above the boiling point of the substance, a stream of vapour rushes through the tube, carrying with it all the air of the globe, if sufficient quantity of the substance had been introduced. When no more vapour is emitted, the point of the tube is sealed before the flame of the blowpipe, the temperature of the bath being observed at the same

moment*, and the globe is removed from the bath, washed, dried, and weighed.

The next point to be determined is the capacity of the globe. For this purpose the neck is broken under the surface of mercury contained in a bason; the metal immediately enters the globe to fill the vacuum caused by the condensation of the vapour at the ordinary temperature, filling the vessel completely, if the operation has been properly conducted. By pouring out the mercury, and measuring it in a graduated jar, the capacity of the globe is ascertained. We thus obtain all the data necessary for the calculation, having determined, experimentally, —

1. The weight of the globe and air at ordinary temperature and pressure;
2. The weight of the globe and vapour filling it at the temperature of the bath, and under ordinary pressure; and,
3. The capacity of the globe.

Having these results, we obtain by calculation, —

1. The weight of the empty globe (by knowing the capacity of the globe, the weight of the air filling it can be calculated, which, deducted from the weight of the globe and air, leaves the weight of the globe when vacuum);
2. The weight of vapour filling the globe at the temperature of the bath (by deducting the weight of the empty globe from the weight of the globe and vapour); and,
3. The weight of air filling the globe at the temperature of the bath, and at the pressure at which the globe was sealed with the vapour.

The last calculation is made according to rules given in the note, page 491.; having performed which, the density of the vapour required is obtained by the simple proportion, — As the weight of air filling the globe at the temperature of the bath is to the weight of vapour filling the globe at the same temperature, so is 1 to the density required.

10. TABLES FOR CALCULATIONS IN ANALYSIS.

In quantitative analysis the substance whose weight is to be determined, instead of being weighed in its free or uncombined state, is more frequently weighed in a state of union with another body, forming a definite compound and one of known composition,

* The globe should be considered to possess a temperature 1° less than that of the bath.

and from the weight of which the weight of the particular constituent whose amount is the object of research is calculated. To facilitate calculations of this kind, the following tables have been constructed to express the quantities of one substance contained in 1·00000, 2·00000, 3·00000, 4·00000, 5·00000, 6·00000, 7·00000, 8·00000, and 9·00000 parts respectively of another substance; and by adding together the proportions corresponding to all the figures in the number which expresses the weight of a substance, the proportion in which one body is contained in or indicated by any amount of another body may be ascertained. The first column, headed "Required," contains the names of the substances whose amounts are to be determined; the second, headed "Found," contains the names of the substances weighed; and the remaining columns, headed by the first nine whole numbers, express the proportions of the "required" substance contained in or indicated by as many parts of the "found" substance as the number at the head of the column. When the number which expresses the quantity of the substance found contains more than one figure as its whole number, the decimal point is advanced in proportion to the right; but if less than one whole number, the decimal point is advanced to the left. The application of these tables will be better comprehended by an example. To find the amount of chlorine contained in 21·34 grains of chloride of silver, proceed as follows:—

| | | | |
|-------|---|-------|--------|
| 20·00 | The number in the column 2, with the decimal point advanced one figure to the right | - | 4·9340 |
| 1· | The number in column 1, without changing the decimal point | - - - | ·2467 |
| ·3 | The number in column 3, with the decimal point advanced one figure to the left | - - | ·0740 |
| ·04 | The number in column 4, with the decimal point advanced two figures to the left | - - | ·0098 |
| <hr/> | | | |
| 21·34 | grains of chloride of silver contain grains of | | |
| | chlorine | - - - | 5·2645 |

Although the idea that the equivalents of all substances are simple multiples of the equivalent of hydrogen seems to be favoured by recent researches on that subject, yet the equivalents upon which the following tables have been constructed generally comprise the decimal numbers in common use, as the equivalents of but few elements have yet been satisfactorily determined to be whole numbers, and if whole numbers are always adopted, such tables as the following are scarcely needful.

| Required. | Foand. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|--|--|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| Aluminum. Al ₂ | Alumina. Al ₂ O ₃ . | 0·53295 | 1·06591 | 1·59886 | 2·13181 | 2·66476 | 3·19772 | 3·73067 | 4·26362 | 4·79658 |
| Ammonia. NH ₃ . | Nitrogen. N. | 1·21147 | 2·42294 | 3·63441 | 4·84588 | 6·05735 | 7·26882 | 8·48029 | 9·69176 | 10·90323 |
| Ammonia. NH ₃ . | Platinum. Pt. | 0·17390 | 0·34780 | 0·52170 | 0·69560 | 0·86950 | 1·04340 | 1·21730 | 1·48120 | 1·56510 |
| Ammonia. NH ₃ . | Chloride of am- monium and pla- tinum. Pt Cl ₂ + NH ₄ Cl. | 0·07693 | 0·15386 | 0·23079 | 0·30772 | 0·38465 | 0·46158 | 0·53851 | 0·61544 | 0·69237 |
| Ammonia. NH ₃ . | Muriate of ammonia. NH ₄ Cl. | 0·32223 | 0·64446 | 0·96669 | 1·28892 | 1·61115 | 1·93338 | 2·25561 | 2·57784 | 2·90007 |
| Antimony. Sb. | Antimony, ox. of. Sb O ₃ . | 0·84317 | 1·68634 | 2·52951 | 3·37268 | 4·21585 | 5·05902 | 5·90219 | 6·74536 | 7·58853 |
| Antimony. Sb. | Antimony, sul- phuret of. Sb S ₂ . | 0·72771 | 1·45542 | 2·18313 | 2·91084 | 3·63855 | 4·36626 | 5·09397 | 5·82168 | 6·54939 |
| Antimony, ox. of. Sb O ₃ . | Antimony, sul- phuret of. Sb S ₃ . | 0·86307 | 1·72614 | 2·58921 | 3·45228 | 4·31535 | 5·17842 | 6·04149 | 6·90456 | 7·76763 |
| Antimony, ox. of. Sb O ₃ . | Antimony. Sb. | 1·18600 | 2·37200 | 3·55800 | 4·74400 | 5·93000 | 7·11600 | 8·30200 | 9·48800 | 10·67400 |
| Arsenic. As. | Arsenic, sul- phuret of. As S ₂ . | 0·60903 | 1·21806 | 1·82709 | 2·43612 | 3·04515 | 3·65418 | 4·26321 | 4·87224 | 5·48127 |
| Arsenic. As. | Arsenic, penta- sulphuret of. As ₂ S ₅ . | 0·48311 | 0·96622 | 1·44933 | 1·93244 | 2·41555 | 2·89866 | 3·38177 | 3·86488 | 4·34799 |

| As γ . | As γ . | As γ . | As γ . | As γ . | As γ . | As γ . | As γ . | As γ . | As γ . | As γ . |
|-------------------|---|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Barium. Ba. | Sulphate of barytes. Ba O + S O ₂ . | 0.58791 | 1.17588 | 1.76382 | 2.35176 | 2.93970 | 3.52764 | 4.11558 | 4.70352 | 5.29146 |
| Barium. Ba. | Barytes. Ba O. | 0.89549 | 1.79099 | .68648 | 3.58198 | 4.47747 | 5.37296 | 6.26846 | 7.16395 | 8.05945 |
| Barytes. Ba J. | Barytes, sulphate of. Ba O, S O ₂ . | 0.65628 | 1.31256 | .6884 | 2.62512 | 3.28140 | 3.93768 | 4.59396 | 5.25024 | 5.90652 |
| Barytes. Ba O. | Barytes, car- bonate of. Ba O, C O ₂ . | 0.77556 | 1.5517 | 2.32758 | 3.10344 | 3.87930 | 4.65516 | 5.43102 | 6.20688 | 6.98274 |
| Barytes. 3 F | Barium, silico- fluoride of. Ba F ₂ + Si ₂ F ₆ . | 0.18297 | 0.36594 | 0.54891 | 0.73188 | 0.91485 | 1.09782 | 1.28079 | 1.46376 | 1.64673 |
| Bismuth. Bi. | Bismuth, oxide of. Bi O. | 0.89867 | 1.79735 | 2.69602 | 3.59470 | 4.49337 | 5.39204 | 6.29072 | 7.18939 | 8.08807 |
| Bromine. Br. | Bromide of silver. Ag Br. | 0.41989 | 0.83978 | 1.25967 | 1.67956 | 2.09945 | 2.51934 | 2.93923 | 3.35912 | 3.77901 |
| Bromine. Br. | Hydrobromic acid. H Br. | 0.98740 | 1.97480 | 2.96220 | 3.94960 | 4.93700 | 5.92440 | 6.91180 | 7.89920 | 8.88660 |
| Calcium. Ca. | Lime. Ca O. | 0.71911 | 1.43823 | 2.15735 | 2.87646 | 3.59558 | 4.31470 | 5.03381 | 5.75293 | 6.47204 |
| Cadmium. Cd. | Cadmium, oxide of. Cd O. | 0.87449 | 1.74899 | 2.62348 | 3.49797 | 4.37246 | 5.24696 | 6.12145 | 6.99594 | 7.87044 |
| Carbon. C. | Carbonic acid. C O ₂ . | 0.27272 | 0.54544 | 0.81816 | 1.09088 | 1.36360 | 1.63632 | 1.90904 | 2.18176 | 2.45448 |

| Required. | Found. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|--|---------|---------|---------|---------|---------|---------|---------|----------|----------|
| Carbon. C. | Cyanogen. C ₂ N ₂ . | 0.46338 | 0.92676 | 1.39014 | 1.85352 | 2.31690 | 2.78028 | 3.24366 | 3.70704 | 4.17042 |
| Carbonic acid. C O ₂ . | Carbonate of lime. Ca O, C O ₂ . | 0.43579 | 0.87158 | 1.30737 | 1.74316 | 2.17895 | 2.61474 | 3.05053 | 3.48632 | 3.92211 |
| Carbonic acid. C O ₂ . | Carbonate of barytes. Ba O, C O ₂ . | 0.22323 | 0.44646 | 0.66969 | 0.89292 | 1.11615 | 1.33938 | 1.56261 | 1.78584 | 2.00907 |
| Chlorine. Cl. | Chloride (sub) of mercury. Hg ₂ Cl. | 0.14883 | 0.29766 | 0.44649 | 0.59532 | 0.74415 | 0.89298 | 1.04181 | 1.19064 | 1.33947 |
| Chlorine. Cl. | Chloride of potassium. K Cl. | 0.47466 | 0.94932 | 1.42398 | 1.89864 | 2.37330 | 2.84796 | 3.32262 | 3.79728 | 4.27194 |
| Chlorine. Cl. | Chloride of silver. Ag Cl. | 0.24670 | 0.49340 | 0.74010 | 0.98680 | 1.23350 | 1.48020 | 1.72690 | 1.97360 | 2.22030 |
| Chlorine. Cl. | Hydrochloric acid. H Cl. | 0.97258 | 1.94516 | 2.91774 | 3.89032 | 4.86290 | 5.83548 | 6.80806 | 7.78064 | 8.75322 |
| Chlorine. Cl. | Chloride of sodium. Na Cl. | 0.60344 | 1.20688 | 1.81032 | 2.41376 | 3.01720 | 3.62064 | 4.22408 | 4.82752 | 5.43096 |
| Chromium. Cr ₂ . | Chromium, oxide of. Cr ₂ O ₃ . | 0.70109 | 1.40217 | 2.10326 | 2.80435 | 3.50543 | 4.20652 | 4.90761 | 5.60800 | 6.30978 |
| Chromic acid. 2(Cr O ₃). | Chromium, oxide of. Cr ₂ O ₃ . | 1.29891 | 2.59782 | 3.89673 | 5.19564 | 6.49455 | 7.79346 | 9.09237 | 10.39128 | 11.69019 |
| Chromic acid. Cr O ₃ . | Chromate of barytes. Ba O, Cr O ₃ . | 0.40518 | 0.81036 | 1.21554 | 1.62072 | 2.02590 | 2.43108 | 2.83626 | 3.24144 | 3.64662 |

| | | | | | | | | | | |
|---|---|---------|---------|---------|---------|---------|----------|----------|----------|----------|
| Copper. Cu. | Copper, protoxide of. Cu O. | 0·79826 | 1·59653 | 2·39479 | 3·19305 | 3·99131 | 4·78958 | 5·58784 | 6·38610 | 7·18437 |
| Copper, suboxide of. $\frac{1}{2}$ (Cu ₂ O). | Copper, protoxide of. Cu O. | 0·89913 | 1·79826 | 2·69739 | 3·59652 | 4·49565 | 5·39478 | 6·29391 | 7·19304 | 8·09217 |
| Cyanogen. C N ₂ . | Cyanide of silver. Ag C ₂ N. | 0·19620 | 0·39240 | 0·58860 | 0·78480 | 0·98100 | 1·17720 | 1·37340 | 1·56960 | 1·76580 |
| Cyanogen. NC ₂ . | Nitrogen. N. | 1·86351 | 3·72702 | 5·59053 | 7·45404 | 9·31755 | 11·18106 | 13·04457 | 14·90808 | 16·77159 |
| Fluorine. F. | Fluoride of calcium. Ca F. | 0·47732 | 0·95464 | 1·43196 | 1·91928 | 2·38660 | 2·86392 | 3·34124 | 3·81856 | 4·29588 |
| Gold. Au ₂ | Gold, oxide of. Au ₂ O ₃ . | 0·89232 | 1·78464 | 2·67696 | 3·56928 | 4·46160 | 5·35392 | 6·24624 | 7·13856 | 8·03088 |
| Gold, oxide of. Au ₂ O ₃ . | Gold. Au ₂ . | 1·12067 | 2·24134 | 3·36201 | 4·48268 | 5·60335 | 6·72402 | 7·84469 | 8·96536 | 10·08603 |
| Hydrochloric acid. H Cl. | Chloride of silver. Ag Cl. | 0·25366 | 0·50732 | 0·76098 | 1·01464 | 1·26830 | 1·52196 | 1·77565 | 2·02928 | 2·28294 |
| Hydrocyanic acid. H C ₂ N. | Cyanide of silver. Ag C ₂ N. | 0·20362 | 0·40724 | 0·61086 | 0·81448 | 1·01810 | 1·22172 | 1·42534 | 1·62896 | 1·83258 |
| Hydrogen. H. | Water. HO: | 0·11111 | 0·22222 | 0·33334 | 0·44445 | 0·55556 | 0·66667 | 0·77778 | 0·88890 | 1·00001 |
| Hypophosphorous acid. PO. | Phosphoric acid. PO ₅ . | 0·55173 | 1·10346 | 1·65519 | 2·20692 | 2·75865 | 3·31038 | 3·86211 | 4·41384 | 4·96557 |

| Required. | Found. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|--|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Iodine. I. | Hydriodic acid. H I. | 0.99216 | 1.98432 | 2.97648 | 3.96864 | 4.96080 | 5.95296 | 6.94512 | 7.93728 | 8.92944 |
| Iodine. I. | Iodide of silver. Ag I. | 0.53868 | 1.07736 | 1.61604 | 2.15472 | 2.69340 | 3.23208 | 3.77076 | 4.30944 | 4.84812 |
| Iodine. I. | Iodide (sub) of copper. Cu ₂ I. | 0.66804 | 1.33208 | 1.99812 | 2.66416 | 3.33020 | 3.99624 | 4.66228 | 5.32882 | 5.99436 |
| Iron. Fe. | Iron, protoxide of. Fe O. | 0.77232 | 1.54464 | 2.31696 | 3.08928 | 3.86160 | 4.63392 | 5.40624 | 6.17856 | 6.95088 |
| Iron. Fe ₂ . | Iron, peroxide of. Fe ₂ O ₃ . | 0.69338 | 1.38677 | 2.08015 | 2.77354 | 3.46692 | 4.16031 | 4.85369 | 5.54708 | 6.24046 |
| Iron, protoxide of. 2 Fe O. | Iron, peroxide of. Fe ₂ O ₃ . | 0.89780 | 1.79560 | 2.69340 | 3.59120 | 4.48900 | 5.38680 | 6.28460 | 7.18240 | 8.08020 |
| Lead. Pb. | Lead, oxide of. Pb O. | 0.92829 | 1.85658 | 2.78487 | 3.71316 | 4.64145 | 5.56974 | 6.49803 | 7.42632 | 8.35461 |
| Lead. Pb. | Lead, sulphate of. Pb O, S O ₃ . | 0.68287 | 1.36574 | 2.04861 | 2.73148 | 3.41435 | 4.09722 | 4.78009 | 5.46296 | 6.14583 |
| Lead. Pb. | Lead, oxide of. Pb O. | 1.07725 | 2.15450 | 3.23174 | 4.30899 | 5.38623 | 6.46348 | 7.54072 | 8.61797 | 9.69521 |
| Lead, chloride of. Pb Cl. | Lead, oxide of. Pb O. | 0.80275 | 1.60550 | 2.40825 | 3.21100 | 4.01375 | 4.81650 | 5.61925 | 6.42200 | 7.22475 |
| Lead, sulphate of. Pb O, S O ₃ . | Lead, oxide of. Pb O. | 0.73563 | 1.47126 | 2.20689 | 2.94252 | 3.67815 | 4.41378 | 5.14941 | 5.88504 | 6.62067 |

| | | | | | | | | | | |
|--|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Lime. Ca O. | Lime, sulphate of. Ca O, S O ₃ . | 0·41532 | 0·83064 | 1·24596 | 1·66128 | 2·07660 | 2·49102 | 2·90724 | 3·32256 | 3·73788 |
| Lime. Ca O. | Lime, carbonate Ca O, C O ₂ . | 0·56292 | 1·12584 | 1·68876 | 2·25168 | 2·81460 | 3·37752 | 3·94044 | 4·50336 | 5·06628 |
| Lithia. 2 Li O. | Lithia, phosphate of soda and. (2Li O + P O ₅) + (2Na O + P O ₅). | 0·12381 | 0·24762 | 0·37143 | 0·49524 | 0·61905 | 0·74286 | 0·86667 | 0·99048 | 1·11429 |
| Magnesium. Mg. | Magnesia. Mg O. | 0·61293 | 1·22587 | 1·83880 | 2·45173 | 3·06466 | 3·67760 | 4·29053 | 4·90346 | 5·51640 |
| Magnesia. 2 Mg O. | Magnesia, phos- phate of. 2Mg O + P O ₅ . | 0·36671 | 0·73342 | 1·10013 | 1·46684 | 1·83355 | 2·20026 | 2·56697 | 2·93368 | 3·30039 |
| Manganese. Mn. | Manganese, prot- oxide of Mn O. | 0·77573 | 1·55147 | 2·32720 | 3·10294 | 3·87867 | 4·65440 | 5·43014 | 6·20587 | 6·98161 |
| Manganese. Mn ₂ . | Manganic oxide. Mn ₂ O ₃ . | 0·69752 | 1·39504 | 2·09256 | 2·79008 | 3·48760 | 4·18512 | 4·88264 | 5·58016 | 6·27768 |
| Manganese. Mn. | Manganese, per- oxide of. Mn O ₂ . | 0·53533 | 1·07106 | 1·60660 | 2·14213 | 2·67766 | 3·21319 | 3·74872 | 4·28426 | 4·81979 |
| Manganese, prot- oxide of. 3 Mn O. | Mangano-man- ganic oxide. Mn O + Mn ₂ O ₃ . | 0·93044 | 1·86088 | 2·79132 | 3·72176 | 4·65220 | 5·58264 | 6·51308 | 7·44352 | 8·37396 |

| Required. | Found. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|---|---------|---------|---------|---------|---------|---------|---------|----------|----------|
| Mercury. Hg ₂ . | Mercury, sub-oxide of. Hg ₂ O. | 0.96200 | 1.92400 | 2.88600 | 3.84800 | 4.81000 | 5.77201 | 6.73401 | 7.69601 | 8.65801 |
| Mercury. Hg. | Mercury, protoxide of. Hg O. | 0.92678 | 1.85357 | 2.78035 | 3.70714 | 4.63392 | 5.56070 | 6.48749 | 7.41427 | 8.34106 |
| Mercury. Hg ₂ . | Mercury, subchloride of. Hg ₂ Cl. | 0.85117 | 1.70234 | 2.55351 | 3.40468 | 4.25585 | 5.10702 | 5.95819 | 6.80936 | 7.66053 |
| Mercury. Hg. | Mercury, sulphuret of. Hg S. | 0.86287 | 1.72574 | 2.58861 | 3.45148 | 4.31435 | 5.17722 | 6.04009 | 6.90296 | 7.76583 |
| Mercury, suboxide of. Hg ₂ O. | Mercury. Hg ₂ . | 1.03950 | 2.07900 | 3.11850 | 4.15800 | 5.19750 | 6.23700 | 7.27650 | 8.31600 | 9.35550 |
| Mercury, protoxide of Hg O. | Mercury. Hg. | 1.07900 | 2.15800 | 3.23700 | 4.31600 | 5.39500 | 6.47400 | 7.55300 | 8.63200 | 9.71100 |
| Mercury, protoxide of. Hg O. | Mercury, sulphuret of. Hg S. | 0.93104 | 1.86208 | 2.79312 | 3.72416 | 4.65520 | 5.58624 | 6.51728 | 7.44832 | 8.37936 |
| Mercury, subchloride of. $\frac{2}{3}$ (Hg ₂ Cl). | Mercury. Hg. | 1.17485 | 2.34970 | 3.52455 | 4.69940 | 5.87425 | 7.04910 | 8.22395 | 9.39880 | 10.57365 |
| Mercury, chloride of. Hg Cl. | Mercury. Hg. | 1.34969 | 2.69938 | 4.04907 | 5.39876 | 6.74845 | 8.09814 | 9.44783 | 10.79752 | 12.14721 |
| Molybdenum. Mo. | Molybdic acid. Mo O ₃ . | 0.66612 | 1.33224 | 1.99836 | 3.66448 | 5.33059 | 6.99671 | 8.66283 | 10.32895 | 11.99507 |
| Molybdenum. Mo. | Molybdenum, tersulphuret of. Mo S ₃ . | 0.49793 | 0.99586 | 1.49379 | 1.99172 | 2.48965 | 2.98758 | 3.48551 | 3.98344 | 4.48137 |

| | | | | | | | | | | |
|---|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Nitric acid. NO ₃ . | Nitrate of barytes Ba O, NO ₅ . | 0.41436 | 0.82872 | 1.24308 | 1.65744 | 2.07180 | 2.48616 | 2.90052 | 3.31488 | 3.72924 |
| Nitric acid. NO ₃ . | Sulphate of barytes. Ba O, SO ₃ . | 0.46434 | 0.92868 | 1.39302 | 1.85736 | 2.32170 | 2.78604 | 3.25038 | 3.71472 | 4.17906 |
| Nitrogen. N. | Cyanogen. C ₂ N. | 0.53662 | 1.07324 | 1.60986 | 2.14648 | 2.86310 | 3.21972 | 3.75634 | 4.29296 | 4.82958 |
| Nitrogen. N. | Platinum. Pt. | 0.14355 | 0.28710 | 0.43065 | 0.57420 | 0.71775 | 0.86130 | 1.00485 | 1.14840 | 1.29195 |
| Oxalic acid. $\frac{1}{2}$ (C ₂ O ₃). | Carbonic acid. C O ₂ . | 0.81818 | 1.63636 | 2.45454 | 3.27272 | 4.09090 | 4.90908 | 5.72726 | 6.54544 | 7.36362 |
| Oxalic acid. $\frac{1}{3}$ (C ₂ O ₃). | Carbonate of lime. Ca O, C O ₂ . | 0.35656 | 0.71312 | 1.06968 | 1.42624 | 1.78280 | 2.13936 | 2.49592 | 2.85248 | 3.20904 |
| Oxygen. O. | Water. HO. | 0.88889 | 1.77778 | 2.66666 | 3.55555 | 4.44444 | 5.33333 | 6.22222 | 7.11110 | 7.99999 |
| Phosphorus. P. | Phosphoric acid. PO ₅ . | 0.43966 | 0.87931 | 1.31897 | 1.75863 | 2.19828 | 2.63794 | 3.07760 | 3.51726 | 3.95691 |
| Phosphoric acid. PO ₅ . | Phosphate of barytes. 2 Ba O+PO ₅ . | 0.31799 | 0.63598 | 0.95397 | 1.27196 | 1.58995 | 1.90794 | 2.22593 | 2.54392 | 2.86191 |
| Phosphoric acid. PO ₅ . | Phosphate of lime. 2 Ca O+PO ₅ . | 0.55618 | 1.11236 | 1.66854 | 2.22472 | 2.78090 | 3.33708 | 3.89326 | 4.44944 | 5.00562 |
| Phosphoric acid. PO ₅ . | Phosphate of lead. 2 Pb O+PO ₅ . | 0.24239 | 0.48478 | 0.72717 | 0.96956 | 1.21195 | 1.45434 | 1.69673 | 1.93912 | 2.18151 |
| Phosphoric acid. | Phosphate of magnesia | 0.63329 | 1.26658 | 1.89987 | 2.53316 | 3.16645 | 3.79974 | 4.43303 | 5.06632 | 5.69961 |

| Required. | Found. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|--|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Phosphorous acid. PO ₃ . | Phosphoric acid. PO ₅ . | 0.77586 | 1.55172 | 2.32758 | 3.10344 | 3.87930 | 4.65516 | 5.43102 | 6.20688 | 6.98274 |
| Platinum. Pt. | Platinum, chloride of potassium and. Pt Cl ₂ + K Cl. | 0.40420 | 0.80840 | 1.21260 | 1.61680 | 2.02100 | 2.42520 | 2.82940 | 3.23360 | 3.63780 |
| Platinum. Pt. | Platinum, chloride of ammonium and. Pt Cl ₂ + NH ₄ Cl. | 0.44232 | 0.88464 | 1.32696 | 1.76928 | 2.21160 | 3.65392 | 3.09624 | 3.53856 | 3.98088 |
| Potassium. K. | Potash K O. | 0.83048 | 1.66097 | 2.49145 | 3.32194 | 4.15242 | 4.98290 | 5.81339 | 6.64387 | 7.47436 |
| Potassium K. | Potassium, chlo- ride of. K Cl. | 0.52534 | 1.05068 | 1.57602 | 2.10136 | 2.62670 | 3.15204 | 3.67738 | 4.20272 | 4.72806 |
| Potassium, chlo- ride of. K Cl. | Silver, chloride of. Ag Cl. | 0.51947 | 1.03894 | 1.55841 | 2.07788 | 2.59735 | 3.11682 | 3.63629 | 4.15576 | 4.67523 |
| Potash. K O. | Potash, sulphate of. K O, SO ₃ . | 0.54067 | 1.08134 | 1.62201 | 2.16268 | 2.70335 | 3.24402 | 3.78469 | 4.32536 | 4.86603 |
| Potash. K O. | Potash, carbonate of. K O, CO ₂ . | 0.68092 | 1.36184 | 2.04276 | 2.72368 | 3.40460 | 4.08552 | 4.76644 | 5.44736 | 6.12828 |
| Potash. K O. | Potassium, chloride of platinum and. Pt Cl ₂ + K Cl. | 0.19334 | 0.38668 | 0.58002 | 0.77366 | 0.96670 | 1.16004 | 1.35338 | 1.54672 | 1.74006 |
| Potash, sulphate of. K O + SO ₃ . | Barytes, sulphate of. Ba O + SO ₃ . | 0.74867 | 1.49734 | 2.24601 | 2.99468 | 3.74335 | 4.49202 | 5.24069 | 5.98936 | 6.73803 |
| Selenium. Se. | Selenious acid. Se O ₂ . | 0.71206 | 1.42411 | 2.13617 | 2.84823 | 3.56028 | 4.27234 | 4.98440 | 5.69646 | 6.40851 |

| | | | | | | | | | | |
|--|--|---------|---------|---------|---------|---------|---------|---------|----------|----------|
| Selenium. S. | Selenium, sul- phuret of. Se S ₂ . | 0.55143 | 1.10286 | 1.65429 | 2.20572 | 2.75715 | 3.30858 | 3.86001 | 4.41144 | 4.96287 |
| Selenious acid. Se O ₂ . | Selenium, sul- phuret of. Se S ₂ . | 0.77442 | 1.54884 | 2.33226 | 3.09768 | 3.87210 | 4.64652 | 5.42094 | 6.19536 | 6.96978 |
| Silver. Ag. | Silver, oxide of. Ag O. | 0.93111 | 1.86222 | 2.79333 | 3.72444 | 4.65555 | 5.58667 | 6.51778 | 7.44889 | 8.38000 |
| Silver. Ag. | Silver, chloride of. Ag Cl. | 0.75330 | 1.50660 | 2.25990 | 3.01320 | 3.76650 | 4.51980 | 5.27310 | 6.02640 | 6.77970 |
| Silver, oxide of. Ag O. | Silver, chloride of. Ag Cl. | 0.80903 | 1.61806 | 2.42709 | 3.23612 | 4.04515 | 4.85418 | 5.66321 | 6.47224 | 7.28127 |
| Soda. Na O. | Soda, sulphate of. Na O, SO ₃ . | 0.43819 | 0.87638 | 1.31457 | 1.75276 | 2.19095 | 2.62914 | 3.06733 | 3.50552 | 3.94371 |
| Soda. Na O. | Sodium, chloride of. Na Cl. | 0.53289 | 1.06578 | 1.59867 | 2.13156 | 2.66445 | 3.19734 | 3.73023 | 4.26312 | 4.79601 |
| Soda. Na O. | Carbonic acid. CO ₂ . | 1.42272 | 2.84544 | 4.26816 | 5.69088 | 7.11360 | 8.53632 | 9.95904 | 11.38176 | 12.80448 |
| Soda, sulphate of. Na O + SO ₃ . | Barytes, sulphate of. Ba O + SO ₃ . | 0.61166 | 1.22332 | 1.83498 | 2.44664 | 3.05830 | 3.66996 | 4.28162 | 4.89328 | 5.50494 |
| Sodium. Na. | Sodium, chloride of. Na Cl. | 0.39656 | 0.79312 | 1.18968 | 1.58624 | 1.98280 | 2.37936 | 2.77592 | 3.17248 | 3.56904 |
| Sodium. Na. | Soda. Na O. | 0.74418 | 1.48836 | 2.23253 | 2.97671 | 3.72089 | 4.46507 | 5.20925 | 5.95342 | 6.69760 |

| Required. | Found. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---------------------------------------|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Sodium, chloride of. Na Cl. | Chloride of silver. Ag Cl. | 0·40876 | 0·81752 | 1·22628 | 1·63504 | 2·04380 | 2·45256 | 2·86132 | 3·27008 | 3·67884 |
| Strontium. Sr. | Strontian. Sr O. | 0·84551 | 1·69102 | 2·53653 | 3·38204 | 4·22755 | 5·07306 | 5·91857 | 6·76408 | 7·60959 |
| Strontian. Sr O. | Strontian, sul- phate of. Sr O, SO ₃ . | 0·56360 | 1·12720 | 1·69080 | 2·25440 | 2·81800 | 3·38160 | 3·94520 | 4·50880 | 5·07240 |
| Strontian. Sr O. | Strontian, car- bonate of. Sr O, CO ₂ . | 0·70074 | 1·40148 | 2·10222 | 2·80296 | 3·50370 | 4·20444 | 4·90518 | 5·60592 | 6·30666 |
| Sulphur. S. | Sulphuret of silver. Ag S. | 0·12955 | 0·25910 | 0·38865 | 0·51820 | 0·64775 | 0·77730 | 0·90685 | 1·03640 | 1·16595 |
| Sulphur. S. | Sulphuret of mercury. Hg S. | 0·13713 | 0·27426 | 0·41139 | 0·54852 | 0·68565 | 0·82278 | 0·95991 | 1·09704 | 1·23417 |
| Sulphur. S. | Sulphuret of copper. Cu S. | 0·33704 | 0·67408 | 1·01112 | 1·34816 | 1·68520 | 2·02224 | 2·35928 | 2·69632 | 3·03336 |
| Sulphur. S. | Sulphate of barites. Ba O, SO ₃ . | 0·13797 | 0·27594 | 0·41391 | 0·55188 | 0·68985 | 0·82782 | 0·96579 | 1·10376 | 1·24173 |
| Sulphur. S. | Sulphate of lead. Pb O, SO ₃ . | 0·10612 | 0·21224 | 0·31836 | 0·42448 | 0·53060 | 0·63672 | 0·74284 | 0·84896 | 0·95598 |
| Sulphurous acid. SO ₂ . | Sulphate of barites. Ba O, SO ₃ . | 0·27514 | 0·55028 | 0·82542 | 1·10056 | 1·37570 | 1·65084 | 1·92598 | 2·20112 | 2·47626 |
| Sulphuric acid. SO ₃ . | Sulphate of barites. Ba O, SO ₃ . | 0·34372 | 0·68744 | 1·03116 | 1·37488 | 1·71860 | 2·06232 | 2·40604 | 2·74976 | 3·09348 |
| Sulphuric acid. SO ₃ . | Sulphate of lime. Ca O, SO ₃ . | 0·58468 | 1·16936 | 1·75404 | 2·33872 | 2·92340 | 3·50808 | 4·09276 | 4·67744 | 5·26212 |

| | | | | | | | | | | |
|--------------------------------------|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Sulphuric acid. SO ₂ . | Sulphate of lead. Pb O, SO ₃ . | 0.26437 | 0.53874 | 0.79311 | 1.05748 | 1.32185 | 1.58622 | 1.85059 | 2.11496 | 2.37933 |
| Tin. Sn. | Tin, peroxide of. Sn O ₂ . | 0.78616 | 1.57233 | 2.35849 | 3.14466 | 3.98082 | 4.71698 | 5.50315 | 6.28931 | 7.07547 |
| Tin, protoxide of. Sn O. | Tin, peroxide of. Sn O ₂ . | 0.89308 | 1.78616 | 2.67924 | 3.57232 | 4.46540 | 5.35848 | 6.25156 | 7.14464 | 8.03772 |
| Titanium. Ti. | Titanic acid. Ti O ₂ . | 0.60293 | 1.20585 | 1.80878 | 2.41171 | 3.01463 | 3.61756 | 4.22049 | 4.82342 | 5.42634 |
| Titanic acid. Ti O ₂ . | Titanium, sul- phuret of. Ti S ₂ . | 0.71342 | 1.42684 | 2.14026 | 2.85368 | 3.56710 | 4.28052 | 4.99394 | 5.70736 | 6.42078 |
| Tungsten. Tu. | Tungstic acid. Tu O ₃ . | 0.79773 | 1.59547 | 2.39320 | 3.19094 | 3.98867 | 4.78641 | 5.58414 | 6.38188 | 7.17961 |
| Uranium. U. | Uranium, per- oxide of. U ₃ O ₅ . | 0.94758 | 1.89515 | 2.84273 | 3.79031 | 4.73788 | 5.68546 | 6.63304 | 7.58062 | 8.52819 |
| Uranium, prot- oxide of. 2 UO. | Uranium, per- oxide of. U ₃ O ₅ . | 0.98252 | 1.96504 | 2.94756 | 3.93008 | 4.91260 | 5.89512 | 6.87764 | 7.86016 | 8.84268 |
| Zinc. Zn. | Zinc, oxide of. Zn O. | 0.80128 | 1.60256 | 2.40385 | 3.20513 | 4.00641 | 4.80769 | 5.60897 | 6.41026 | 7.21154 |

TABLE OF ATOMIC WEIGHTS.

| Name. | Symbol. | Atomic Weight. |
|------------------------------|--------------------------|----------------|
| Alumina - - - - | $\text{Al}_2 \text{O}_3$ | 51.44 |
| Aluminum - - - - | Al | 13.72 |
| Ammonia - - - - | N H_3 | 17.19 |
| Antimony - - - - | Sb | 129.24 |
| oxide of - - - - | Sb O_3 | 153.28 |
| sulphuret of - - - - | Sb S_3 | 177.6 |
| Arsenic - - - - | As | 75.34 |
| sulphuret of - - - - | As S_4 | 123.7 |
| sulphuret of - - - - | As S_5 | 155.94 |
| Arsenic acid - - - - | As O_5 | 115.34 |
| Arsenious acid - - - - | As O_3 | 99.34 |
| Barium - - - - | Ba | 68.66 |
| chloride of (dry) - - - - | Ba Cl | 207.0 |
| Barytes - - - - | Ba O | 76.66 |
| carbonate of - - - - | Ba O, CO_2 | 98.88 |
| phosphate of - - - - | 2 Ba O, PO_5 | 224.76 |
| sulphate of - - - - | Ba O, SO_3 | 116.78 |
| Bismuth - - - - | Bi | 71.07 |
| Boron - - - - | B | 10.91 |
| Bromine - - - - | Br | 78.39 |
| Cadmium - - - - | Cd | 55.83 |
| Calcium - - - - | Ca | 20.52 |
| chloride of (dry) - - - - | Ca Cl | 55.98 |
| Carbon - - - - | C | 6.0 |
| Carbonic acid - - - - | CO_2 | 22.0 |
| Carbonic oxide - - - - | CO | 14.0 |
| Cerium - - - - | Ce | 46.05 |
| Chlorine - - - - | Cl | 35.47 |
| Chromium - - - - | Cr | 28.19 |
| Cobalt - - - - | Co | 29.57 |
| Colombium (tantalum) - - - - | Ta | 184.9 |
| Copper - - - - | Cu | 31.71 |
| protoxide of - - - - | Cu O | 39.71 |
| suboxide of - - - - | $\text{Cu}_2 \text{O}$ | 71.42 |
| Fluorine - - - - | F | 18.74 |
| Glucium - - - - | G | 26.54 |
| Gold - - - - | Au | 199.21 |
| Hydrogen - - - - | H | 1.0 |
| Iodine - - - - | I | 126.57 |
| Iridium - - - - | Ir | 98.84 |
| Iron - - - - | Fe | 27.18 |
| peroxide of - - - - | $\text{Fe}_2 \text{O}_3$ | 78.36 |
| protoxide of - - - - | Fe O | 35.18 |
| Lead - - - - | Pb | 103.73 |
| carbonate of - - - - | Pb O, CO_2 | 133.89 |
| chloride of - - - - | Pb Cl | 139.2 |
| phosphate of - - - - | 2 Pb O, PO_5 | 294.9 |
| protoxide of - - - - | Pb O | 111.73 |
| sulphate of - - - - | Pb O, SO_3 | 151.9 |

TABLE OF ATOMIC WEIGHTS—*continued.*

| Name. | Symbol. | Atomic Weight. |
|------------------------------|---|----------------|
| Lime - - - - | Ca O | 28.52 |
| carbonate of - - - - | Ca O, CO ₂ | 50.52 |
| sulphate of - - - - | Ca O, SO ₃ | 68.64 |
| Lithium - - - - | L | 6.44 |
| Magnesia - - - - | Mg O | 20.69 |
| sulphate of - - - - | Mg O, SO ₃ | 60.81 |
| Magnesium - - - - | Mg | 12.69 |
| Manganese - - - - | Mn | 27.72 |
| protoxide of - - - - | Mn O | 35.72 |
| deutoxide of - - - - | Mn ₂ O ₃ | 79.44 |
| Mercury - - - - | Hg | 101.43 |
| subchloride of - - - - | $\frac{1}{2}$ (Hg ₂ Cl) | 119.16 |
| oxide of - - - - | Hg O | 109.43 |
| suboxide of - - - - | Hg ₂ O | 210.86 |
| Molybdenum - - - - | Mo | 47.96 |
| Nickel - - - - | Ni | 29.62 |
| Nitrogen - - - - | N | 14.19 |
| Osmium - - - - | Os | 99.72 |
| Oxygen - - - - | O | 8.0 |
| Palladium - - - - | Pd | 53.36 |
| Phosphoric acid - - - - | PO ₅ | 71.44 |
| Phosphorous acid - - - - | PO ₃ | 55.44 |
| Phosphorus - - - - | P | 31.44 |
| Platinum - - - - | Pt | 98.84 |
| ammonia-chloride of - - - - | { (Pt Cl ₂ + NH ₄ Cl) | 224.44 |
| potassio-chloride of - - - - | { (Pt Cl ₂ + K Cl) | 244.51 |
| Potash - - - - | KO | 47.26 |
| carbonate of - - - - | KO, CO ₂ | 69.42 |
| sulphate of - - - - | KO, SO ₃ | 87.43 |
| Potassium - - - - | K | 39.26 |
| chloride of - - - - | K Cl | 74.7 |
| Rhodium - - - - | R | 52.20 |
| Selenium - - - - | Se | 39.63 |
| Silicon - - - - | Si | 22.22 |
| Silver - - - - | Ag | 108.30 |
| chloride of - - - - | Ag Cl | 143.77 |
| oxide of - - - - | Ag O | 116.3 |
| Soda - - - - | Na O | 31.31 |
| carbonate of - - - - | Na O, CO ₂ | 53.47 |
| sulphate of - - - - | Na O, SO ₃ | 71.48 |
| Sodium - - - - | Na | 23.31 |
| chloride of - - - - | Na Cl | 58.78 |
| Strontian - - - - | Sr O | 51.85 |
| carbonate of - - - - | Sr O, CO ₂ | 73.85 |
| sulphate of - - - - | Sr O, SO ₃ | 91.97 |
| Strontium - - - - | Sr | 43.85 |
| chloride of - - - - | Sr Cl | 79.32 |

TABLE OF ATOMIC WEIGHTS—*continued.*

| Name. | Symbol. | Atomic Weight. |
|-----------------------|-----------------|----------------|
| Sulphur - - - - | S | 16·12 |
| Sulphuric acid - - - | S O_3 | 40·12 |
| Sulphurous acid - - - | S O_2 | 32·12 |
| Tellurium - - - - | Te | 64·25 |
| Thorium - - - - | Th | 59·83 |
| Tin - - - - | Sn | 58·92 |
| peroxide of - - - | Sn O_2 | 74·92 |
| protoxide of - - - | Sn O | 66·92 |
| Titanium - - - - | Ti | 24·33 |
| Tungsten - - - - | W | 94·80 |
| Uranium - - - - | U | 217·26 |
| Vanadium - - - - | V | 68·66 |
| Water - - - - | HO | 9·0 |
| Yttrium - - - - | Y | 32·25 |
| Zinc - - - - | Zn | 32·31 |
| oxide of - - - - | Zn O | 40·31 |
| Zirconium - - - - | Zr | 33·67 |

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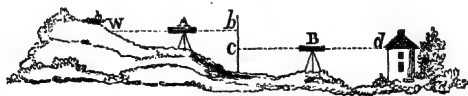
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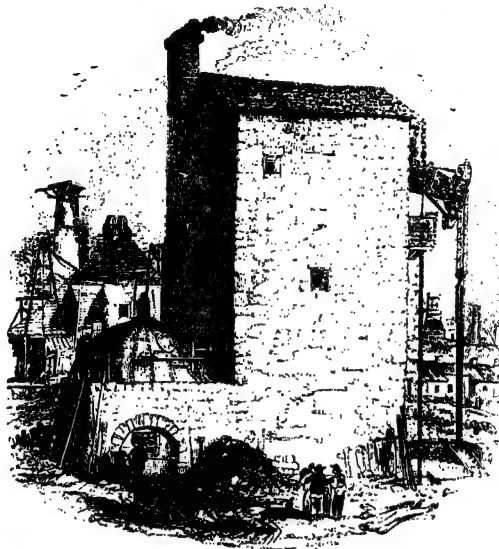
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